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POLYTHIONIC ACIDS

V. NEW DATA ON SELENOPOLYTHIONATES. PREPARATION OF POTASSIUM DISELENOTETRATHIONATE

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The selenopolythionic acids are polythionic acids in which the sulfur has been partially replaced by selenium. Up to now they have not been known in the free state, but some of their salts are known. The salt potassium selenotrithionate $K_2SeS_2O_6$ [1] was obtained even in the previous century, to the anion of which has been ascribed the role of intermediate substance in the catalytic decomposition of bisulfite under the influence of selenium [2]. Recently Foss [3] succeeded in obtaining the selenopentathionate $Na_2SeS_4O_6 \cdot 3H_2O$ and the analogous salts of potassium, rubidium, cesium and ammonia [4]. The selenotetrathionates, i.e., salts of the hypothetical tetrathionic acids, in which the sulfur has been partially replaced by selenium, up to now have not been described in the literature, although some authors have expressed opinions on the existence of such compounds [5, 6]. Also unknown are the selenopolythionates with more than one selenium atom in the molecule.

In the present paper we communicate the results of the experiments which led us to the establishment of new reactions for the formation and decomposition of the selenotrithionate, and also for the preparation of the previously unknown potassium diselenotetrathionate.

1. Catalytic decomposition of the selenotrithionate under the influence of the iodide ion. The spontaneous decomposition of the selenotrithionate radical in aqueous solution, proceeding in accord with the equations [2, 5],

$$SeS_2O_6^{''} + H_2O \longrightarrow SO_4^{''} + SeSO_3^{''} + 2H^{\cdot}, \quad (1)$$

$$SeSO_3^{''} + 2H^{\cdot} \longrightarrow Se + SO_2 + H_2O, \quad (2)$$

is quite a slow process. For example, in 0.05 M $K_2SeS_2O_6$ solution the amount of selenotrithionate after the lapse of 14 hours at room temperature drops by only 2% [3].

In acidified selenotrithionate solution the same decomposition proceeds somewhat faster, but in acid solution it is markedly accelerated in the presence of potassium iodide, i.e., in the presence of the iodide ion, which plays the role of catalyst here. For example, a 0.01-0.02 M $K_2SeS_2O_6$ solution with an equivalent amount of HCl and 2 g/liter of KI was allowed to stand overnight at room temperature. The result was complete decomposition of the selenotrithionate. In the same solution without the addition of KI only about 9% of the selenotrithionate underwent decomposition in the same length of time.

The mechanism of the catalytic action of the iodide ion can be judged from the following qualitative experiment. A concentrated $K_2SeS_2O_6$ solution is acidified with 2 N HCl, then some starch solution is added and several milliliters of 10% KI solution.

Almost instantly a blue color appears, which vanishes after 0.5-1 second; simultaneously the rapid separation of red selenium begins.

This experiment leaves no doubt that here the first stage of the reaction is the oxidation of the iodide ion to iodine, which then in turn oxidizes any other decomposition product of the selenotrithionate. If it is assumed that the selenium in the selenotrithionate ion is bivalent and positive, for which a number of foundations exist [3], then the first stage of the reaction can be expressed by the equation

$$H_2[Se(SO_3)_2] + 2I^{'} \longrightarrow Se + 2HSO_3^{'} + I_2. \quad (3)$$

The liberated iodine oxidizes the bisulfite:

$$HSO_3^- + I_2 + H_2O \longrightarrow HSO_4^- + 2HI. \quad (4)$$

Combining these two equations gives the complete equation for the catalytic decomposition of the selenotrithionate:

$$H_2[Se(SO_3)_2] + H_2O \longrightarrow Se + H_2SO_3 + H_2SO_4. \quad (5)$$

The same complete equation is obtained by combining Equations (1) and (2), i.e., for the decomposition of the selenotrithionate in the absence of catalyst. But in this case the whole process proceeds very slowly, and at elevated temperature is accompanied by as yet obscure secondary reactions [5]; consequently, we subjected Equation (5) for the catalytic decomposition of the selenotrithionate to quantitative verification.

The starting substance for our experiments was pure $K_2SeS_2O_6$, prepared by the method of Foerster and Haufe [2]. A control analysis by the Foss method [3] gave a selenium content of 24.9% (calculated from the formula, 24.98% Se).

The experiments were run as follows. The weighed $K_2SeS_2O_6$ (ca. 10 mg-mol) was dissolved in a 250 ml volumetric flask in an equivalent amount (20 mg-mol) of 0.5 N or 0.2 N HCl, 5 ml of 10% KI solution was added, the flask was stoppered tightly and allowed to stand at room temperature. When 0.5 N HCl is used the reaction is complete in 1 hour, the liberated selenium settles, and the solution can be subjected to analysis. If 0.2 N HCl is taken, about 3 hours is required for completion of the reaction and settling of the selenium.

For analysis the solution is made up to volume. The selenium again quickly settles; then from the top, clear layer a pipetted sample is removed for the iodometric determination of sulfurous acid. The sample titrated with iodine is then titrated with 0.2 N sodium hydroxide solution. Since in the oxidation of sulfurous acid with iodine free hydriodic acid is formed:

$$H_2SO_3 + I_2 + H_2O \longrightarrow H_2SO_4 + 2HI, \quad (6)$$

then here the consumption of alkali should be 6 equivalents for 1 mole of taken selenotrithionate. Another sample of the solution is poured into the exactly calculated amount of iodine solution needed for oxidation of the sulfurous acid, and here the total amount of sulfur is determined gravimetrically as $BaSO_4$. The usual oxidation with bromine is inexpedient in the given case due to the presence of the iodide ion. Subtraction of the iodometrically found sulfurous acid from the total amount of sulfur gives the amount of sulfuric acid formed as the result of selenotrithionate decomposition. This amount of sulfuric acid can also be found from the results of the alkali and iodine titrations; however, we preferred the gravimetric method for the determination of total sulfur, in view of its greater accuracy.

The experimental data (Table 1) show that the iodide ion catalyzed decomposition of the selenotrithionate proceeds quantitatively in accord with Equation (5). The somewhat low values obtained for sulfurous acid are explained by the volatility of SO_2.

TABLE 1

Catalytic Decomposition of the Selenotrithionate

Expt. No.	Taken (mg-mol)		Concentration of HCl (in N)	Found (mg-mol)			
	$K_2SeS_2O_6$	HCl		$SO_3^{=}$	$SO_4^{=}$	H^+	Se*
1	10.00	20.00	0.5	9.3	10.2	59.0	–
2	10.10	20.00	0.5	9.55	9.9	58.9	10.22
3	10.03	20.00	0.2	9.6	10.2	59.5	10.09
4	10.00	20.00	0.2	9.0	–	59.5	10.10

Subsequently, we used this reaction for the quantitative determination of sulfur in the selenotrithionate. For this purpose, in order to avoid SO_2 losses by volatilization, it is expedient to decompose the acidified selenotrithionate solution immediately with ordinary iodine solution, containing iodide, with subsequent titration of the remaining iodine with thiosulfate. As a result, the determined sulfite sulfur represents, in accord with Equation (5), half of the total sulfur of the selenotrithionate.

2. Oxidation of the selenosulfate with iodine. The selenosulfates are formed when elementary selenium is dissolved in concentrated solutions of sulfites [1, 5]. The formation and decomposition of the selenosulfate in accord with the equation $Na_2SO_3 + Se \rightleftharpoons Na_2SeSO_3$ is used for the purification of selenium [7].

* Determined gravimetrically (in mg-atoms).

In aqueous solution, the selenosulfate is stable only in the presence of an excess of free alkali or a considerable amount of sulfite [5]. When its solution is titrated with iodine the selenosulfate usually cleaves selenium and is oxidized to the sulfate, i.e., it titrates like sulfite [1, 6].

In the search for a rapid and convenient method for the quantitative determination of the selenosulfate in admixture with sulfite we made a number of attempts to find the conditions under which the selenosulfate could be titrated with iodine in a manner analogous to the titration of thiosulfate, i.e., in accord with the hypothetical equation

$$2SeSO_3^{--} + I_2 \longrightarrow Se_2S_2O_6^{--} + 2I' \qquad (7)$$

These experiments led to the following result. If the sample (5-10 ml) of solution, containing the selenosulfate and sulfite, previously diluted to 200 ml, is rapidly poured into a dilute neutral solution of iodine (also made up to 200 ml) and the residual iodine titrated very rapidly with thiosulfate, then the liberation of selenium is retarded, and the consumption of iodine actually occurring is considerably less than in the usual titration, in which the sample is poured into an acidified solution of iodine, which leads to the instantaneous liberation of selenium. Since the oxidation of the sulfite in accord with Equation (6) requires twice as much iodine as does the oxidation of the selenosulfate in accord with Equation (7), the difference in the expenditures of iodine in the two titrations should correspond to the amount of selenosulfate in the analyzed solution.

Here we do not present the numerical data for these experiments, since the quantitative determination of the selenosulfate by this method fails to give satisfactory results: the found amount of selenosulfate is usually lower by 10-20%, while the reproducibility of the analyses leaves a better method to be desired. However, these experiments left no doubt as to the fact that the oxidation of the selenosulfate is also possible without the liberation of selenium, i.e., that it apparently leads under certain conditions to products other than the sulfate, and specifically, to the formation of the hypothetical diselenotetrathionate in accord with Equation (7). This caused us to undertake a further study of the oxidation of the selenosulfate.

Recently Foss found that the titration of the selenotrithionate with iodine in bicarbonate solution results in its oxidation to the selenite and sulfate [3]. We found that the selenosulfate also gives the same end products when oxidized with iodine in bicarbonate medium. But if the titration of the mixture of the selenosulfate with sulfite* is not carried to the end, but is terminated after the expenditure of 1-1.5 equivalents of iodine per 1 mole of $SeSO_3^{--} + SO_3^{--}$, then the selenite is not formed, selenium is not liberated, but the selenosulfate disappears. When the solution obtained in this manner is acidified with 2 N hydrochloric acid there is observed the appearance and almost instantaneous disappearance of iodine, and then the slow liberation of red selenium and sulfur dioxide. This, as was shown above, is a typical reaction for the selenotrithionate – its catalytic decomposition with iodine in acid medium.

From this the conclusion is offered that in the titration of a mixture of the selenosulfate and sulfite with iodine in bicarbonate medium the product first formed is the selenotrithionate. It can be assumed that the reaction proceeds in accord with the scheme

$$2SeSO_3^{--} + I_2 \longrightarrow Se_2S_2O_6^{--} + 2I' \qquad (7)$$

$$Se_2S_2O_6^{--} + SO_3^{--} \longrightarrow SeS_2O_6^{--} + SeSO_3^{--} \qquad (8)$$

$$SeSO_3^{--} + SO_3^{--} + I_2 \longrightarrow SeS_2O_6^{--} + 2I' \qquad (9)$$

TABLE 2

Verification of Equation (9)

Expt. No.	Taken (mg-mol)			Found (mg-mol)
	K_2SeSO_3	K_2SO_3	I_2	$K_2SeS_2O_6$
5	0.735	0.715	0.735	0.733
6	0.735	0.715	0.735	0.749

To verify this assumption, we subjected a mixture of the selenosulfate and sulfite to oxidation with iodine, proceeding from the ratio of the reactants derived from Equation (9).

The experimental data (Table 2) show that Reaction (9) proceeds in bicarbonate medium practically quantitatively.

The experiments were made in the following manner. To a solution (10 ml), containing the amounts of selenosulfate and sulfite indicated in Table 2, was added 0.5 g of $KHCO_3$ and the calculated amount of 0.05 N iodine solution. Then 0.2 N H_2SO_4 was added to barely acid reaction (pH ≈4). Here no liberation of selenium was observed, which indicates the complete disappearance of the selenosulfate. Then more of the same H_2SO_4 was added in an amount equivalent to the taken selenosulfate, i.e., the expected selenotrithionate, and the solution was allowed to stand overnight in a stoppered flask for the complete

* The presence of sulfite is necessary to avoid decomposition of the selenosulfate with the cleavage of selenium.

decomposition of the selenotrithionate in accord with Equation (5). After this the solution was titrated with iodine and then with 0.1 N caustic solution, as described above. The amounts of formed selenotrithionate given in Table 2 were found from the expenditure of alkali.

Reaction (9) proceeds so smoothly under the indicated conditions that it can be used for the preparation of crystalline potassium selenotrithionate.

To 5 ml of solution, containing 3.68 mg-mol of K_2SeSO_3 and the same amount of K_2SO_3, are added 2 g of $KHCO_3$ and the calculated amount (18.5 ml) of 0.4 N iodine solution. Then to avoid contamination of the product with bicarbonate, 5 ml of 10% acetic acid is added, the mixture is shaken (to remove CO_2), cooled to 0°, and diluted with 150 ml of alcohol. Needle-like crystals of $K_2SeS_2O_3$ separate, which are rapidly filtered and washed with alcohol. Yield – above 1 g (ca. 85%). A single recrystallization of these crystals gives a completely pure selenotrithionate.

Found %: Se 24.80, 24.76. $K_2SeS_2O_3$. Calculated %: Se 24.95.

3. Oxidation of the selenosulfate with hydrogen peroxide. In our scheme for the formation of the selenotrithionate from the selenosulfate and sulfite in accord with Equation (9) the primary process is the hypothetical oxidation of the selenosulfate with iodine to the diselenotetrathionate in accord with Equation (7). If this scheme is valid, then the replacement of the iodine by some other oxidizing agent should lead to the same end reaction products; consequently, we next undertook the study of the action of hydrogen peroxide on a mixture of the selenosulfate with sulfite. If the analogy to the action of iodine holds, it can be expected that here the reaction will proceed in accord with the scheme

$$2SeSO_3^{--} + H_2O_2 + 2H^+ \longrightarrow Se_2S_2O_6^{--} + 2H_2O \quad (10)$$

$$Se_2S_2O_6^{--} + SO_3^{--} \longrightarrow SeS_2O_6^{--} + SeSO_3^{--} \quad (8)$$

$$SeSO_3^{--} + SO_3^{--} + H_2O_2 + 2H^+ \longrightarrow SeS_2O_6^{--} + 2H_2O \quad (11)$$

The replacement of iodine by hydrogen peroxide also made it possible to plan with greater probability on obtaining the supposed intermediate product – the previously unknown diselenotetrathionate, since hydrogen peroxide fails to give, other than water, any other reduction products, and it also excludes the above-described catalytic action of the iodide ion.

The reaction of hydrogen peroxide with the mixture of selenosulfate and sulfite proceeds very violently with the liberation of a large amount of heat. When a large excess of H_2O_2 is used against the amount required for Equation (11) it is possible to distinguish two clearly defined phases of the reaction. The first phase proceeds without the liberation of selenium, and the evolution of heat is temporarily arrested. Then, after the lapse of a certain induction period ranging from several seconds to 15-20 minutes (depending on the concentration of the solution), the solution begins to foam strongly and selenium is deposited, which later partially dissolves again. The final solution in this case contains the selenite and the sulfate; consequently, only the first phase of the reaction is of interest here, which it is possible to realize separately, without the separation of selenium, by using the amount of hydrogen peroxide required for Equation (11), or with a slight excess of it.

TABLE 3

Action of Hydrogen Peroxide on a Solution of Selenosulfate and Sulfite

Expt. No.	Taken (mg-mol)			Precipitate obtained		Analysis of precipitate (%)		Analysis of recrystallized precipitate (%)	
	K_2SeSO_3	K_2SO_3	H_2O_2	g	yield on Se (%)	Se	S	Se	S
7	17.3	12.9	15.1	1.62	28.1	24.1	20.0	24.7	–
8	19.6	8.9	16.0	1.59	24.7	24.3	20.2	24.7	20.4
9	8.65	6.45	15.1	1.61	47.3	20.0	15.5	–	–
10	19.6	8.9	28.5	2.69	41.1	23.6	18.5	25.0	20.4
Calculated for $K_2SeS_2O_6$						24.95	20.22	24.95	20.22

The original solutions were prepared by dissolving selenium in 3 M K_2SO_3 solution. To the exactly measured amount of such a solution, containing the amounts of selenosulfate and sulfite indicated in Table 3, was added 6-8 N H_2O_2 dropwise and with cooling. Subsequent cooling with an ice-NaCl mixture gave a white needle-like precipitate of $K_2SeS_2O_6$, which can be recrystallized from water.

From the experimental data (Table 3) it can be seen that the action of hydrogen peroxide on the mixture of selenosulfate and sulfite actually leads to the formation of the selenotrithionate. However, here the yield of the latter is considerably less than in the oxidation with iodine. Apparently, here part of the hydrogen peroxide is consumed for the secondary reaction – the oxidation of the sulfite to sulfate. This is indicated, first, by some contamination of the obtained selenotrithionate with sulfate (for example, in Experiments 9 and 10); second, by the fact that when a somewhat reduced amount of hydrogen peroxide is used (Experiments 7 and 8), a considerable portion of the selenosulfate remains unreacted (instantaneous separation of selenium when the solution is acidified). The use of a certain excess of hydrogen peroxide, against the amount required for Equation (11) (Experiments 9 and 10), leads to complete disappearance of the selenosulfate, but here also the yield of selenotrithionate is small.

The reduction in the yield of selenotrithionate when compared with the previous experiments, where iodine was used as the oxidizing agent, can be explained by the fact that here we took the selenosulfate in excess of the 1:1 ratio with sulfite required for Equation (11). Consequently, and also because of the partial oxidation of the sulfite to sulfate, a considerable portion of the hypothetical diselenotetrathionate, constituting, in our opinion, the primary oxidation product of the selenosulfate, could have been retained in the solution unchanged.

4. Preparation of potassium diselenotetrathionate. The above-presented experimental results on the preparation of the selenotrithionate by the oxidation of a mixture of selenosulfate and sulfite with hydrogen peroxide caused us to expect that from the mother liquors, remaining after the separation of the major portion of the selenotrithionate, it would be possible to obtain the still hypothetical diselenotetrathionate. Our experiments revealed that this became possible if the method of fractional crystallization from acidified solution was used.

To 20 ml of solution, containing 35 mg-mol of K_2SeSO_3 and not more than 20 mg-mol of K_2SO_3, cooled and stirred, was added dropwise 5 ml of 7.8 M H_2O_2. Then, with cooling to room temperature, was immediately added 20 ml of 2 N HCl. Here the solution acquires a greenish-yellow color. After the addition of 50 ml of alcohol there immediately begins the separation of a white precipitate, which is filtered after standing for 30 minutes at 8-10°. This 1st fraction is the selenotrithionate, contaminated with sulfate. From the mother liquor after standing for 3 hours in the refrigerator there separate yellow needle-like crystals (1.6-1.7 g) of the potassium diselenotetrathionate, somewhat contaminated by the selenotrithionate and sulfate (2nd fraction). For purification this product was dissolved in the minimum amount of 0.5 N HCl, warmed to 30-40°, quickly filtered through a dry filter and cooled in an ice-NaCl mixture. The obtained crystals were washed with alcohol and ether, and air-dried in the dark. These crystals are the crystallohydrate $K_2Se_2S_2O_8 \cdot H_2O$ (Preparations I and II, Table 4). When dried at elevated temperature (50-60°) the anhydrous salt $K_2SeS_2O_8$ (Preparations III and IV) was obtained. However, at elevated temperature the crystals partially turned slightly red on the surface (cleavage of Se).

TABLE 4

Analysis of Potassium Diselenotetrathionate

Preparation No.	Found						Calculated for	
	I	II	III	IV	V	VI	$K_2Se_2S_2O_8 \cdot H_2O$	$K_2Se_2S_2O_8$
% Se . . .	37.9	37.9	39.15	39.4	38.75	38.85	38.26	39.90
% S	15.7	15.6	16.25	16.2	16.4	16.35	15.46	16.19
% K	–	–	–	–	19.9	19.65	18.89	19.75
% H_2O. . .	4.5	4.45	–	–	–	–	4.35	–

The formation of the diselenotetrathionate by the action of hydrogen peroxide on the selenosulfate, which we express by the simple Equation (10), is probably a more complex process. This is indicated by the fact that the characteristic yellow color of the diselenotetrathionate appears in the synthesis only when the solution is acidified, while the heat is liberated for the most part even prior to acidification.

The oxidation of the selenosulfate is not the only method for the formation of the diselenotetrathionate. Again Foerster and Seidel [5] found that a dilute solution of the selenotrithionate when heated evolves SO_2 and acquires a yellow color. They postulated that among the decomposition products of the selenotrithionate under these conditions the diselenotetrathionate is also formed.

Our experiments, performed on more concentrated solutions of $K_2SeS_2O_8$ and under somewhat different conditions, confirmed this postulate of the mentioned authors. Not dwelling on the experimental details, since in view of the small yield this method cannot be recommended for the preparation of the diselenotetrathionate, we will only mention that with this method we obtained preparations containing about 36% of Se and 16% of S, i.e., $K_2Se_2S_2O_8$, contaminated with the selenotrithionate and sulfate.

Apparently here the formation of the diselenotetrathionate proceeds as the result of the reactions:

$$SeS_2O_6^{--} + H_2O \longrightarrow SO_4^{--} + SeSO_3^{--} + 2H^+, \quad (1)$$

$$SeS_2O_6^{--} + SeSO_3^{--} + 2H^+ \rightleftharpoons Se_2S_2O_6^{--} + SO_2 + H_2O. \quad (12)$$

Equation (12), analogous to Equation (8), proceeds from right to left. In support of such a treatment speaks the fact that the removal of SO_2 by the passage of air, or even better, of CO_2 through the acidified selenotrithionate solution, as our experiments revealed, facilitates the formation of the diselenotetrathionate.

From the preparative viewpoint not bad results are obtained by the combination of the two methods for the formation of the diselenotetrathionate, i.e., by the oxidation of the selenosulfate with hydrogen peroxide in the presence of sulfite, and subsequent partial decomposition of the formed selenotrithionate.

To 25 ml of solution, containing 50 mg-mol of K_2SeSO_3 and 23 mg-mol of K_2SO_3, cooled, was added dropwise 6 ml of 7.8 M H_2O_2, then 25 ml of water and immediately 50 ml of 2 N HCl. Then carbon dioxide gas was passed for about 3 hours at 25-30°, which removed most of the liberated SO_2; in this connection the separation of selenium should not begin; if it does begin, the passage of CO_2 should be quickly terminated. Then 100 ml of alcohol was added, the mixture was cooled, and the obtained precipitate, the selenotrithionate contaminated with sulfate, was filtered. To the mother liquor was added another 200 ml of alcohol and 100 ml of ether and again the mixture was strongly cooled. After 1-2 hours the obtained yellow crystals of $K_2Se_2S_2O_6 \cdot H_2O$ admixed with $K_2SeS_2O_6$ and K_2SO_4 were filtered. Yield about 7 g. As described above, purification was effected by recrystallization from 0.5 N HCl.

The analysis results for the preparations, obtained in this manner and dried at 50-60°, are given in Table 4 (Preparations V and VI).

Potassium diselenotetrathionate was obtained as yellow needle-like crystals, readily soluble in water. In neutral aqueous solution this compound gradually decomposes with the liberation of selenium. Acidification of the solution markedly raises the stability, but sulfurous acid lowers it. When the solution is made alkaline the yellow color disappears and selenium is liberated. But in the presence of a considerable amount of selenotrithionate, for example, prior to the separation of the first precipitate fraction in the synthesis, the separation of selenium from the $K_2Se_2S_2O_6$ solution when made alkaline, fails to occur.

When sufficiently pure, the $K_2Se_2S_2O_6$ is quite stable in the dry form, but it is sensitive to ordinary daylight, which after only a few days causes a reddening of the originally pure yellow crystals, which is the first sign of incipient decomposition.

Analogous to the selenotrithionate, under the influence of the iodide ion in acid medium the diselenotetrathionate undergoes catalytic decomposition, and specifically, in accord with the equation

$$H_2Se_2S_2O_6 + H_2O \longrightarrow Se_2 + H_2SO_3 + H_2SO_4. \quad (13)$$

This reaction can be used for the quantitative analysis of $K_2Se_2S_2O_6$ preparations: the weighed sample is dissolved in dilute HCl, an excess of ordinary iodine solution is added, the remainder of which is back-titrated with thiosulfate. From the consumption of iodine for the oxidation of the sulfurous acid, formed in accord with Equation (13), is calculated the total amount of polythionate sulfur in the sample.

The validity of this method, and consequently of Equation (13), is confirmed by the fact that we determined sulfur in a number of preparations (for example, Preparations V and VI, Table 4) by this method, and also by the usual gravimetric method (as $BaSO_4$). Both methods gave completely similar results.

Reaction (13) explains the impossibility of iodometrically determining the selenosulfate when it is in admixture with the sulfite (see above). Since the oxidation of the sulfite in accord with Equation (6) gives free hydrogen and iodine ions, it leads to the decomposition of the diselenotetrathionate formed in accord with Equation (7), which decomposition slowly proceeds also in highly dilute solution.

SUMMARY

1. It was established that the decomposition of the selenotrithionate radical in acid medium is catalytically accelerated by the iodide ion and quantitatively proceeds in the presence of this catalyst in accord with Equation (5).

2. The action of iodine on a mixture of selenosulfate and sulfite in bicarbonate solution leads to the formation of the selenotrithionate in accord with Equation (9).

3. The selenotrithionate is also formed by the oxidation of a mixture of selenosulfate and sulfite with hydrogen peroxide.

4. In the oxidation of the selenosulfate the product first formed is the diselenotetrathionate in accord with the equation $2SeSO_3^{=} - 2e \rightarrow Se_2S_2O_6^{=}$.

5. As crystalline salts of the hypothetical diselenotetrathionic acid the compounds potassium diselenotetrathionate $K_2Se_2S_2O_6$ and its crystallohydrate $K_2Se_2S_2O_6 \cdot H_2O$ were obtained for the first time. The diselenotetrathionate is also formed in the decomposition of the selenotrithionate.

6. In the presence of the iodide ion the diselenotetrathionate in acid medium is catalytically decomposed in accord with Equation (13).

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STUDY OF METAL NITRIDES

III.* PHASE DIAGRAM OF THE SYSTEM Ba–N IN THE REGION OF HIGH PRESSURES

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In 1951 it was shown by us [1] that together with the peroxides of the alkaline earth metals there also exist the pernitrides – the higher nitrogen compounds of these elements, and specifically, we synthesized barium pernitride, BaN_2, the existence of which was predicted by the isoatom method of S. A. Shchukarev [2].

In the interest of determining the number of phases in the system barium-nitrogen we undertook the tensimetric investigation of the decomposition process for barium pernitride. The apparatus used for this purpose consisted of a high pressure bomb, having a volume of about 16 ml, supplied with a finger-like well for the thermocouple and connected to a high pressure steel pipe with a three-way pipe, on which were mounted a fine regulation valve and a standard Class 0.35 manometer with a 0-500 kg/cm^2 scale.

The bomb was contained in a muffle furnace and was surrounded by a thin-walled asbestos tube with nichrome wire winding. This spiral was included in the circuit through a photorelay, which was governed by a mirror galvanometer serving as the null instrument of the potentiometric scheme used for the e.m.f. measurement of the chromel-copel thermocouple, the hot junction of which rested on the bottom of the well, found halfway along the bomb length. The bomb was completely filled with barium pernitride, and into it was introduced nitrogen which had been carefully purified for several days in a large autoclave with lithium nitride (at 450-500° C). Then the selected experimental temperature was set (maintained with an accuracy of $\pm$ 0.5°), at which temperature the preparation was kept for about a day under nitrogen pressure conditions that were considerably higher than the equilibrium pressure (found approximately in prior orientating experiments).

Then the pressure was reduced and its subsequent change was observed. A constant pressure for 4 hours was considered as a sign that equilibrium had been attained.

After equilibrium had been established the pressure was reduced to the original reading; in this connection the gas was exhausted into a volumetric cylinder and its volume was measured. The decomposition product had the composition corresponding to Ba_3N_2.

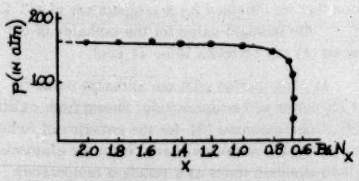

Fig. 1. Relation between the nitrogen equilibrium pressure (in atm) and the composition of the solid phase at 466° C.

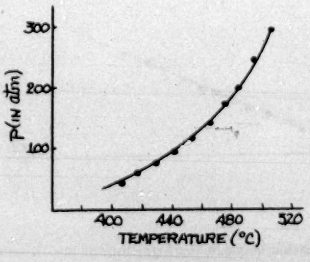

Fig. 2. Relation between the dissociation pressure of barium pernitride (in atm) and the temperature.

* Communication II see [1].

Naturally, from the volume of evolved nitrogen it was possible to determine the composition of the preparation at its different decomposition stages.

For verification the bomb in a number of cases was overheated by several degrees, the pressure was noticeably increased, then the temperature was reduced and the decrease in pressure was observed. Equilibrium at 400-500° C was established in 10-16 hours.

The decomposition isotherm for BaN_2, obtained at 466° C, is given in Fig. 1, from which it can be seen that the equilibrium

$$3BaN_2 \rightleftharpoons Ba_3N_2 + 2N_2$$

is univariant. No intermediate thermodynamically stable phases between BaN_2 and Ba_3N_2 are observed.

The relation between the nitrogen pressure and the temperature, corresponding to the equilibrium (1), is given in the table and in Fig. 2.

t (in °C)	pN_2 (in atm)
395.5	35.6
407	46.4
418.5	59.9
429.5	75.7
442	93.7
454	115.4
466	140.2
476	169.2
486.5	209.4
496.5	254.2
507	295.3

The relation between the logarithm of the nitrogen equilibrium pressure and the reciprocal of the absolute temperature is given in Fig. 3, from which it can be seen that the experimental points fall very well on a straight line. The use of the obtained relationship between the nitrogen equilibrium pressure and the temperature in the well-known thermodynamic equation $-2RT \ln pN_2 = \Delta H - T\Delta S$, with the assumption that the values ΔH and ΔS are constant in the investigated temperature range leads to the following values for the change in the enthalpy and entropy accompanying the process (1):

$$\Delta H_{451^\circ C} = 38.1 \text{ kcal.} \quad \Delta S_{451^\circ C} = 71.1 \text{ kcal/1°.}$$

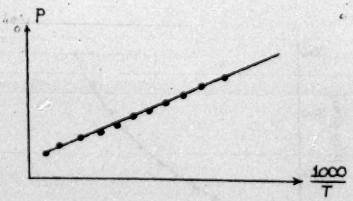

Fig. 3. Relation between the logarithm of the dissociation pressure for barium pernitride (in atm) and the reciprocal of the absolute temperature.

The heat capacities of barium nitride and barium pernitride are not known, consequently it is impossible to find the exact value for the change in the enthalpy of the examined process at a standard temperature, but it can be assumed that it will not differ by more than 2-4 kcal from the value that we obtained for a temperature of 451° C i.e., the standard value for the enthalpy of the process (1) can be taken to be 41 kcal.

In combination with the enthalpy value for the formation of barium nitride, known from calorimetric measurements [3], for the enthalpy of formation of barium pernitride, BaN_2, from the elements in their standard states at a standard temperature of 291° K and a pressure of 1 atm, on the basis of the data obtained by us, it is possible to assume that: $\Delta H_{298} = -43.6$ kcal/mole.

$$Ba_{cryst} + N_{2gas} = BaN_{2cryst.} + 43.6 \text{ kcal.}$$

By the isoatom method of S. A. Shchukarev this value was calculated by us to be 38 kcal/mole, which is close to the experimentally found value.

As a result, the isoatom method of S. A. Shchukarev is the simplest and most trustworthy way of estimating the enthalpy values for the formation of inorganic compounds when compared with all of the other methods known to us.

SUMMARY

1. It was established that the equilibrium $3BaN_2 \rightleftharpoons Ba_3N_2 + 2N_2$ is univariant.

2. The relation between the dissociation pressure of barium pernitride and the temperature was established in the temperature range 395.5-507° C.

3. On the basis of tensimetric measurements the enthalpy for the formation of barium pernitride (BaN_2) is equal to −43.6 kcal/mole.

The experimentally obtained value for the enthalpy of formation of barium pernitride lies close to the value predicted by the isoatom method of S. A. Shchukarev.

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Leningrad State University

• See Consultants Bureau Translation, page 609.

PREPARATION OF THE SIMPLER SODIUM THIOSULFATOARGENTATES

G. A. Garkusha

As we had communicated earlier [1], the salt $Na_5[Ag(S_2O_3)_3]$ (I) in its stability in aqueous solutions, and also in the dry state, sharply differs from the sodium thiosulfatoargentates known in the literature. To confirm its structure as a complex salt, we prepared the barium salt (II) in accord with the equation

$$2Na_5[Ag(S_2O_3)_3] + 9BaCl_2 \longrightarrow Ba_5[Ag(S_2O_3)_3]_2 + 18NaCl.$$

The analysis data confirmed the composition of salt (II), while its yield, close to the theoretical, confirmed the course of the reaction in the indicated direction.

Of the two simpler sodium thiosulfatoargentates – $NaAgS_2O_3 \cdot H_2O$ (III) and $Na_3[Ag(S_2O_3)_2]$ (IV) – the latter is readily soluble in water, so we also prepared its barium salt (V) in accord with the equation

$$2Na_3[Ag(S_2O_3)_2] + 3BaCl_2 \longrightarrow Ba_3[Ag(S_2O_3)_2]_2 + 6NaCl.$$

The salts (V) and (II) are difficultly soluble in water – in the ratio of 1:4000, while the solubility of BaS_2O_3 is equal to 1:480.

From a comparison of (I), (III) and (IV) the existence of the salts $Na_5[Ag(S_2O_3)_3]$ (VI) and $Na_7[Ag(S_2O_3)_4]$ (VII) could be postulated. Actually, by the action of the corresponding number of moles of sodium thiosulfate on salt (IV) we obtained these salts in accord with the equations:

$$Na_3[Ag(S_2O_3)_2] + Na_2S_2O_3 \longrightarrow Na_5[Ag(S_2O_3)_3],$$

$$Na_3[Ag(S_2O_3)_2] + 2Na_2S_2O_3 \longrightarrow Na_7[Ag(S_2O_3)_4].$$

From these salts the barium salts were obtained:

$Ba_5[Ag(S_2O_3)_3]_2$ (VIII) and $Ba_7[Ag(S_2O_3)_4]_2$ (IX).

It should be mentioned that salt (VI) in aqueous solutions proved to be less stable than salts (VII) and (I). It was exactly this property that explained the failures in the experiments where decomposition of the reaction solution was observed either from its long standing in the cold or when the temperature was raised slightly above 45°, in those cases where less than the calculated amount of sodium thiosulfate was taken.

On comparing the formulas of the examined series of simpler sodium thiosulfatoargentates it can be seen that each salt can be obtained from the insoluble salt (III) by the action of the proper number of moles of sodium thiosulfate with the removal of water from the reaction solution. This method is not suitable for salt (IV), since the removal of water even at room temperature for a period of several hours leads to decomposition of the reaction solution. It should be noted that salts (I), (VI) and (VII) can be obtained by starting from an ammoniacal solution of silver (I), but their yields are considerably lower due to the use of alcohol for precipitating the reaction product, and also the use of 70% alcohol for removing the saltpeter formed as a by-product.

In general these salts were obtained by us in accord with the equations:

$$NaAgS_2O_3 + 2Na_2S_2O_3 \longrightarrow Na_5[Ag(S_2O_3)_3],$$

$$NaAgS_2O_3 + 3Na_2S_2O_3 \longrightarrow Na_7[Ag(S_2O_3)_4],$$

$$NaAgS_2O_3 + 4Na_2S_2O_3 \longrightarrow Na_9[Ag(S_2O_3)_5].$$

The barium salts, obtained from these sodium salts by the above indicated reactions, corresponded to the above given formulas.

For the preparation of salts (I), (VI) and (VII) a prolonged heating of the reaction solutions was required. The removal of the water of crystallization from these salts made it much easier for us to study them.

EXPERIMENTAL*

Preparation of sodium trithiosulfatoargentate (VI). To a solution of 55 g of $Na_2S_2O_3 \cdot 5H_2O$ in 30 ml of water was added at 40° in portions and with stirring 26.1 g of salt (III) (calculated as 100%). The reaction solution was filtered through a Buchner funnel, poured into a dish and allowed to stand at room temperature until the following day. Water was removed by heating at not above 40° with stirring until a white precipitate appeared. Then the evaporation was conducted on the water bath at such a heating rate that there was more precipitate and less mother liquor in the dish, and the temperature was not raised above 50°. The congealed mass weighing 56 g was dissolved in the minimum amount of water and after several filtrations the completely clear solution was poured into a dish and the water was removed as formerly. The cream-colored mass, solid at 50°, was heated with successive elevation of the temperature to 60, 70 and 80° without effecting liquefaction. The removal of the water of crystallization was terminated when the cream color of the precipitate became snow-white. A constant weight of 50.2 g (90%) was obtained by drying at 90-95°.

Found %: S_2O_3 59.9, 59.8; Ag 18.8, 18.5. $Na_3[Ag(S_2O_3)_2]$. Calculated %: S_2O_3 60.2; Ag 19.3.

Twenty grams of salt (VI) was dissolved in 10 ml of water and 25 ml of 10% $BaCl_2$ solution was added with stirring. The precipitate depositing and separating from the mother liquor after several hours was filtered and washed with water to complete removal of chloride ion, and then was washed 5 times with alcohol. The solubility of the salt, dried at 100-105°, in water at 20° was 1:4000 (stirring for not less than 1 hour).

Found %: Ag 13.0, 12.6; Ba 43.37, 43.4. $Ba_3[Ag(S_2O_3)_2]_2$. Calculated %: Ag 13.7; Ba 43.57.

The amount of S_2O_3 in salt (III) was determined by the titration of a weighed sample in an exact volume of 0.1 N sodium thiosulfate solution with 0.1 N iodine solution.

If 4.0 g of salt (IV) and 2.5 g of $Na_2S_2O_3 \cdot 5H_2O$ in 2.5 ml of water are taken for reaction with subsequent precipitation of the reaction product with alcohol (not less than 10 ml), then 4.12 g (75%) of salt (VI) is obtained.

Preparation of sodium tetrathiosulfatoargentate (VII). To 75 g of $Na_2S_2O_3 \cdot 5H_2O$ in 45 ml of water is added with stirring at room temperature 26.1 g (calculated as 100%) of salt (III) to complete solution. The filtered reaction solution was treated in the same manner as indicated above for the preparation of salt (VI). After recrystallization, the snow-white crystals, dehydrated at 90-95°, had a constant weight of 70 g (93.5%). Their solubility in water was about 1:1 (20°). The aqueous solutions of the salt are stable under room temperature conditions for a period of several days, as well as on heating up to 80° for about 30 minutes.

Found %: S_2O_3 62.5, 62.7; Ag 14.8, 14.7. $Na_3[Ag(S_2O_3)_4]$. Calculated %: S_2O_3 62.48; Ag 15.05.

The barium salt (IX) was obtained as was indicated above. Its solubility in water is about 1:4000 (20°).

Found %: Ag 9.9, 9.74; Ba 45.6, 45.5. $Ba_3[Ag(S_2O_3)_4]_2$. Calculated %: Ag 10.4; Ba 46.4.

Salt (VII), separated from the reaction solution by the method of alcohol precipitation, was obtained in a yield of 70% of theory.

Found %: S_2O_3 61.8, 61.4; Ag 14.8, 14.7. $Na_3[Ag(S_2O_3)_4]$. Calculated %: S_2O_3 62.48; Ag 15.05.

If to a solution of 3.4 g of silver nitrate in 3 ml of water and 4 ml of 25% NH_3 there is added at room temperature 20 g of $Na_2S_2O_3 \cdot 5H_2O$ and from the filtered reaction solution the water is removed, as indicated above, and then the obtained snow-white precipitate is dissolved in the minimum amount of water and the crystals are precipitated by the addition of 2 volumes of alcohol, they will contain saltpeter. To remove the latter, the precipitate is stirred with 70% alcohol to a fluid mass, and the mass is filtered and washed with 70% alcohol and alcohol to remove traces of saltpeter (test with diphenylamine). Weight of dehydrated crystals 10.0 g (70%).

Found %: S_2O_3 61.6, 61.8; Ag 14.65, 14.8. $Na_3[Ag(S_2O_3)_4]$. Calculated %: S_2O_3 62.48; Ag 15.05.

Preparation of sodium pentathiosulfatoargentate (I). To a solution of 40 g of $Na_2S_2O_3 \cdot 5H_2O$ in 20 ml of water was added at 40° with stirring 10.5 g (calculated as 100%) of salt (III) and then further treatment was the same as for the preparation of salt (VI). Weight of snow-white crystals, dehydrated at 90-95°, was 32.02 g (91%). The solubility and stability of the salt in aqueous solutions almost corresponded to that of salt (VII).

Found %: S_2O_3 63.2, 62.8; Ag 11.95, 11.3. $Na_3[Ag(S_2O_3)_2]$. Calculated %: S_2O_3 64.2; Ag 12.35. Found %: Ag 8.35, 8.25; Ba 47.4, 47.2. $Ba_3[Ag(S_2O_3)_2]_2$. Calculated %: Ag 8.4; Ba 48.0.

* E. Ya. Karaulova participated in the analytical work.

The treatment of a solution of 3.4 g of silver nitrate in 3 ml of water with 4 ml of 25% NH_3 and 25 g of $Na_2S_2O_3 \cdot 5H_2O$, with subsequent separation of salt (I) in accord with the preparation of salt (VII), also gave 14.0 g (80%) of snow-white crystals.

Found %: S_2O_3 62.9, 63.2; Ag 11.6, 11.7. $Na_3[Ag(S_2O_3)_2]$. Calculated %: S_2O_3 64.2; Ag 12.35.

The barium salt (V) was obtained in the same manner as salt (VIII).

Found %: Ag 19.5, 19.8; Ba 37.6, 37.9. $Ba_3[Ag(S_2O_3)_2]_2$. Calculated %: Ag 20.09; Ba 38.34.

SUMMARY

1. New methods for the preparation of the salt $Na_5[Ag(S_2O_3)_3]$ have been proposed, which methods have been extended to the unknown salts $Na_5[Ag(S_2O_3)_3]$ and $Na_7[Ag(S_2O_3)_4]$.

2. The unknown salts were obtained: $Ba_3[Ag(S_2O_3)_2]_2$, $Ba_5[Ag(S_2O_3)_3]_2$, $Ba_7[Ag(S_2O_3)_4]_2$ and $Ba_9[Ag(S_2O_3)_5]_2$.

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REACTIONS OF ALKALI AND ALKALINE EARTH CHLORIDES IN MELTS

I. TERNARY SYSTEM OF SODIUM, RUBIDIUM AND CALCIUM CHLORIDES

V. E. Plyushchev, F. V. Kovalev, and I. V. Shakhno

The analysis of considerable literature material on binary salt systems, made by S. D. Gromakov [1], permitted the elucidation of a number of rules, on the basis of which the qualitative characterization of unstudied types of phase diagram systems could be predicted.

The actual experimental studies of S. D. Gromakov [2] show a good agreement with the found rules, in which number is included the case of the reactions of binary alkali and alkaline earth salt mixtures in melts. Making use of these rules it is possible, as was shown by S. D. Gromakov [3], to make a critical evaluation of already studied systems.

The elucidation of a series of rules in the formation of binary salt systems is exclusively based on complex formation. The formation of chemical compounds in salt systems is regarded, for example, from the viewpoint of the influence of cations on the energy of formation of compounds [4], although it must be assumed that complex formation is not the only criterion in solving the question as to the types of binary systems and as to the reaction character of salts in melts.

As regards ternary salt systems, here the basic obstacle in the path of systematizing and generalizing the data relating to them is the extreme paucity of factual material. It is sufficient to indicate, for example, that of 45 possible ternary systems, formed from alkali and alkaline earth chlorides, judging from the literature data only 6 were studied; in this connection some of these systems were studied in a highly orientating manner. The study of the reaction of alkali and alkaline earth salts in melts was directed to the end that some sort of solution to the existing problem be achieved.

The present paper is part of this study and is devoted to a study of the equilibrium in melts of sodium, rubidium and calcium chlorides.

The binary systems forming the given ternary system have already been described in the literature.

The system NaCl–RbCl was studied by S. Zhemchuzhny and F. Rambakh [5]. The fusion diagram consists of two branches, intersecting at the eutectic point, corresponding to 54.96 mole % of RbCl and 541°. No transformations whatsoever in the solidus region.

The system NaCl–$CaCl_2$ was first studied by Menge [6], who believed that the compound having the composition $4NaCl \cdot CaCl_2$ and melting with decomposition at 605° was formed. The eutectic point corresponds to 32% by weight of NaCl and 500°.

Menge, proceeding from different thermal effects, apparently due to non-uniform crystallization in the system, also believed the formation in the system of solid solutions on the basis of NaCl to be possible, but later investigations [7] failed to support the fusion diagram proposed by him.

According to the data of A. M. Pichugina [8], the system NaCl–$CaCl_2$ belongs to the simple eutectic type; the eutectic melts at 494° and 52.9 mole % of $CaCl_2$.

The system RbCl–$CaCl_2$ was first studied by S. D. Gromakov [2]. The data obtained by him indicate the presence in the system of the chemical compound $RbCl \cdot CaCl_2$, melting without decomposition at 840°. With the original components of the system this compound gives the eutectics: first – 17.5 mole % of $CaCl_2$ and 580°, second – 82.5 mole % of $CaCl_2$ and 680°.

According to E. P. Dergunov and A. G. Bergman [9] the chemical compound in the system RbCl–$CaCl_2$ has the same composition, but melts without decomposition at 930°; the eutectic $RbCl \cdot CaCl_2$ with RbCl has m.p. 630°; the eutectic $RbCl \cdot CaCl_2$ with $CaCl_2$ melts at 696°.

The noticeable differences between the two investigations and the lack of agreement in the crystallization temperatures of the melts, noted by us in studying the yields of the sections of the ternary system on the given binary, made it necessary to check the system $RbCl-CaCl_2$.

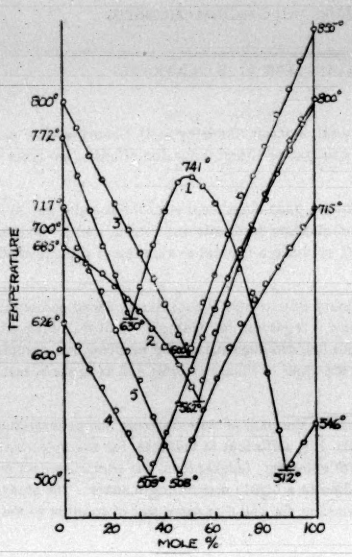

Fig. 1. Fusion curves for the sections of the ternary system. 1) $CaCl_2$ → 55% RbCl + 45% NaCl; 2) 80% $CaCl_2$ + 20% RbCl → → NaCl; 3) NaCl → 50% RbCl + 50% $CaCl_2$; 4) 80% RbCl + + 20% $CaCl_2$ – NaCl; 5) RbCl – 80% NaCl + 20% $CaCl_2$.

It was established that the compound $RbCl \cdot CaCl_2$ melts at 855°, while the eutectics, respectively, correspond to 17.5 and 82.5 mole % of $CaCl_2$ and 580 and 678°. As a result, our data are in good agreement with the investigations of S. D. Gromakov.

EXPERIMENTAL

The system $NaCl-RbCl-CaCl_2$ was studied by the visual-polythermal method in the usual manner.

The starting substances for the preparation of the pure components of the system were chemically pure NaCl, RbCl and $CaCl_2 \cdot 6H_2O$.

The first two chlorides were recrystallized three times from water and dried; the crystallohydrate of calcium chloride was dehydrated by heating, and then by fusion with a constant passage of dry hydrogen chloride to prevent appreciable oxide formation. The amount of calcium oxide in the anhydrous preparation obtained in this manner failed to exceed 0.06%.

Taking into consideration the hygroscopicity of calcium chloride, we used the technique of adding exactly weighed portions of the other two components to the melt of calcium chloride or to the melt of intermediate composition, which permitted us to obtain more reliable results. A total of 11 sections was studied, the scheme of which is given on the diagram for the isotherms of the liquidus surface (Fig. 4). Sections 10 and 11 were drawn parallel to two sides of the triangle, and the composition of their points along one of the components was constant. These sections were selected to bring out the character of the liquidus surface in the region of high concentrations of RbCl and $CaCl_2$.

The character of the studied sections of the ternary system can be seen from Figs. 1-3, while the experimental data relating to them are given in Tables 1-4.

The compositions, characterizing the points of the sections, are always expressed in mole percents. The values, given in the columns, were obtained graphically.

SUMMARY

1. The reactions of the molten chlorides of sodium, rubidium and calcium were studied by the visual-polythermal method.

2. The isotherms for the liquidus surface of the system sodium chloride-rubidium chloride-calcium chloride were constructed.

3. The existence of four fields of crystallization in the system was established: three being pure components and the fourth being the field of crystallization of the binary compound $RbCl \cdot CaCl_2$; the formation of a chemical compound at the ternary junction was not observed.

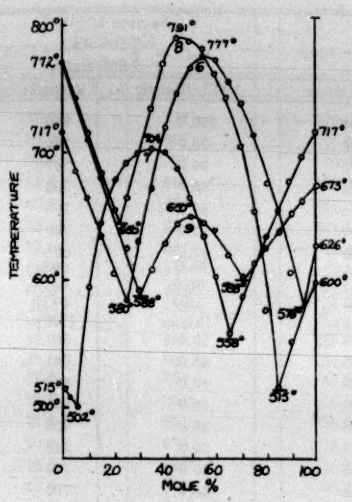

Fig. 2. Fusion curves for the sections of the ternary system. 6) RbCl → 70% $CaCl_2$ + 30% NaCl; 7) 47% NaCl + 53% $CaCl_2$ → RbCl; 8) $CaCl_2$ → 70% RbCl + 30% NaCl; 9) $CaCl_2$ → 70% NaCl + 30% RbCl.

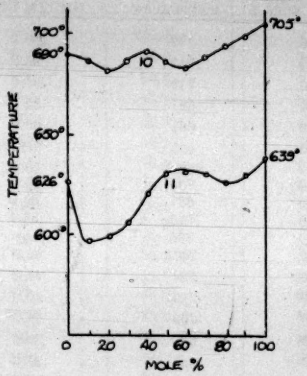

Fig. 3. Fusion curves for the sections of the ternary system. 10) 15% RbCl + 85% $CaCl_2$ → 15% NaCl + 85% $CaCl_2$; 11) 20% $CaCl_2$ + 80% RbCl → 20% NaCl + + 80% RbCl.

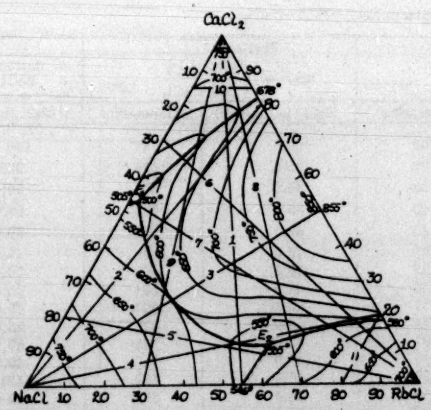

Fig. 4. Isotherms for the liquidus surface of the system NaCl–RbCl–$CaCl_2$ with the diagram of the studied sections.

TABLE 1

Sections 1, 2 and 3 of the System NaCl–RbCl–$CaCl_2$

Section 1 $CaCl_2$ → {45% NaCl, 55% RbCl}		Section 2 NaCl → {20% RbCl, 80% $CaCl_2$}		Section 3 NaCl → {50% RbCl, 50% $CaCl_2$}	
$CaCl_2$ (in mole %)	temperature	NaCl (in mole %)	temperature	NaCl (in mole %)	temperature
100.0	772°	100.0	800°	100.0	800°
95.0	743	95.0	786	95.0	780
90.0	715	90.0	770	90.0	757
85.0	687	85.0	744	85.0	738
80.0	663	80.0	725	80.0	720
75.0	635	75.0	697	75.0	700
(74)	(630)	70.0	669	70.0	681
70.0	655	65.0	641	65.0	663
65.0	687	60.0	617	60.0	641
60.0	715	55.0	580	55.0	617
55.0	736	(54)	(562)	(51)	(600)
50.0	741	50.0	576	50.0	607
45.0	734	45.0	592	45.0	641
40.0	720	40.0	608	40.0	663
35.0	700	35.0	622	35.0	697
30.0	678	30.0	636	30.0	725
25.0	649	25.0	645	25.0	743
20.0	585	20.0	655	20.0	766
15.0	542	15.0	668	15.0	788
(11.6)	(512)	10.0	672	10.0	809
10.0	516	5.0	677	5.0	831
5.0	533	0.0	685	0.0	855
0.0	546				

TABLE 2

Sections 4, 5 and 6 of the System NaCl–RbCl–$CaCl_2$

Section 4 NaCl → {80% RbCl, 20% $CaCl_2$}		Section 5 RbCl → {80% NaCl, 20% $CaCl_2$}		Section 6 RbCl → {30% NaCl, 70% $CaCl_2$}	
NaCl (in mole %)	temperature	RbCl (in mole %)	temperature	RbCl (in mole %)	temperature
100.0	800°	100.0	717°	100.0	717°
95.0	782	95.0	686	95.0	687
90.0	762	90.0	667	90.0	665
85.0	743	85.0	650	85.0	636
80.0	723	80.0	618	80.0	605
75.0	703	75.0	605	75.0	580
70.0	683	70.0	582	70.0	631
65.0	660	65.0	554	65.0	674
60.0	637	60.0	527	60.0	720
55.0	614	55.0	508	55.0	748
50.0	587	50.0	533	50.0	766
45.0	562	45.0	556	45.0	776
40.0	539	40.0	582	(43)	(777)
35.0	515	35.0	605	40.0	793
(34)	(509)	30.0	631	35.0	756
30.0	520	25.0	644	30.0	739
25.0	539	20.0	657	25.0	715
20.0	557	15.0	670	20.0	675
15.0	575	10.0	683	15.0	635
10.0	590	5.0	698	10.0	604
5.0	607	0.0	715	(5.5)	(578)
0.0	626			5.0	582
				0.0	626

TABLE 3

Sections 7, 8 and 9 of the System NaCl–RbCl–$CaCl_2$

Section 7: RbCl → {47% NaCl, 53% $CaCl_2$}		Section 8: $CaCl_2$ → {30% NaCl, 70% RbCl}		Section 9: $CaCl_2$ → {70% NaCl, 30% RbCl}	
RbCl (in mole %)	temperature	$CaCl_2$ (in mole %)	temperature	$CaCl_2$ (in mole %)	temperature
100.0	717°	100.0	772°	100.0	772°
95.0	697	95.0	743	95.0	743
90.0	677	90.0	715	90.0	715
85.0	655	85.0	680	85.0	683
80.0	633	80.0	656	80.0	657
75.0	613	(77.5)	(650)	75.0	627
70.0	587	75.0	665	70.0	594
65.0	558	70.0	700	(69)	(588)
60.0	602	65.0	735	65.0	608
55.0	635	60.0	770	60.0	630
50.0	665	55.0	790	55.0	645
45.0	689	(52.5)	(791)	50.0	650
40.0	701	50.0	786	45.0	645
35.0	704	45.0	780	40.0	637
30.0	701	40.0	762	35.0	620
25.0	691	35.0	743	30.0	603
20.0	678	30.0	705	(29)	(598)
15.0	645	25.0	655	25.0	613
10.0	590	20.0	575	20.0	625
5.0	506	(15.5)	515	15.0	640
4.5	502	15.0	(517)	10.0	653
2.5	508	10.0	552	5.0	663
0.0	515	5.0	580	0.0	673
		0.0	600		

TABLE 4

Sections 10 and 11 of the System NaCl–RbCl–$CaCl_2$

Section 10: {15% RbCl, 85% $CaCl_2$} → {15% NaCl, 85% $CaCl_2$}			Section 11: {80% RbCl, 20% $CaCl_2$} → {80% RbCl, 20% NaCl}		
NaCl (in mole %)	RbCl (in mole %)	temperature	NaCl (in mole %)	$CaCl_2$ (in mole %)	temperature
0.0	15.0	690°	0.0	20.0	626°
1.5	13.5	687	2.0	18.0	597
3.0	12.0	682	4.0	16.0	600
4.5	10.5	687	6.0	14.0	606
6.0	9.0	692	8.0	12.0	621
7.5	7.5	686	10.0	10.0	632
9.0	6.0	684	12.0	8.0	632
10.5	4.5	689	14.0	6.0	630
12.0	3.0	695	16.0	4.0	626
13.5	1.5	699	18.0	2.0	630
15.0	0.0	705	20.0	0.0	639

4. The existence in the system of two eutectic points was noted, corresponding to the melting points 500° (E_1) and 505° (E_2), to them correspond the compositions: E_1 – 2.5 mole % RbCl, 45 mole % NaCl and 52.5 mole % $CaCl_2$; and E_2 – 11.2 mole % $CaCl_2$, 32.8 mole % NaCl and 56.0 mole % RbCl.

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TERNARY RECIPROCAL SYSTEM OF LITHIUM AND POTASSIUM SULFATES AND TUNGSTATES

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As the result of studying the given system it was established that the compounds formed on the side binary systems $Li_2WO_4-K_2WO_4$ and $Li_2SO_4-K_2SO_4$ determine the fundamental character of the system and shift the exchange equilibrium in the direction of the formed stable section of both complexes: $Li_2WO_4 \cdot K_2WO_4-Li_2SO_4 \cdot K_2SO_4$ (Fig. 1). This section in the reciprocal system Li, K | SO_4, WO_4 is triangular and has the character of a simple eutectic system with a transition point of 512°. It makes a composition square on two tetragons, each of which in turn is subjected to triangulation on two phases of the triangle. Similar reciprocal systems are called reciprocal systems of the "belt type" [1], and the system Li, K ‖ SO_4, WO_4 studied by us is a real example of an adiagonal belt type of reciprocal system.

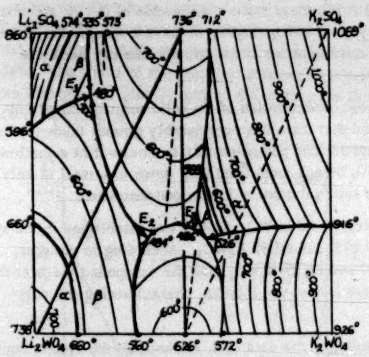


Fig. 1. Projection of the space diagram of the system on the composition square (E_1 480°, E_2 484°, E_3 486°; P 526°).

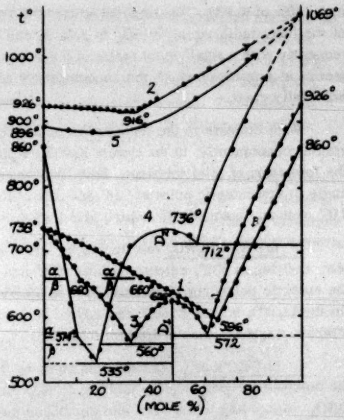


Fig. 2. Sides of the square of the reciprocal system. 1) $Li_2WO_4-Li_2SO_4$; 2) $K_2WO_4-K_2SO_4$; 3) $Li_2WO_4-K_2WO_4$; 4) $Li_2SO_4-K_2SO_4$; $D_1 \rightarrow Li_2WO_4 \cdot K_2WO_4$; $D_2 \rightarrow Li_2SO_4 \cdot K_2SO_4$; 5) data of Amadori [2].

EXPERIMENTAL

Method of operation. The study was made by the visual-polythermal method in a platinum crucible with platinum stirrer and using a Pt, Rh−Pt, Au, Pd thermocouple with an extremely sensitive galvanometer. The liquidus curves were determined from the temperatures of first crystal appearance. The lithium and potassium tungstates were synthesized from tungsten trioxide and freshly precipitated carbonates, in their turn prepared from recrystallized chlorides. The melting points of the pure components were taken as: K_2WO_4 926°, Li_2WO_4 738°, K_2SO_4 1069°, Li_2SO_4 860°.

TABLE 1

Sides and Diagonal Sections of the Reciprocal System

Binary systems and diagonal sections	Original component	M.p. of original component	Added component	Branches of crystallization and their intersection points					
				branch 1	intersection of 1 and 2		branch 2	intersection of 2 and 3	
					% *	t°		% *	t°
$Li_2WO_4-Li_2SO_4$	Li_2WO_4	738°	Li_2SO_4	α-Li_2WO_4	37.5	660°	β-Li_2WO_4	68	596°
$Li_2WO_4-K_2WO_4$	Li_2WO_4	738	K_2WO_4	α-Li_2WO_4	14	660	β-Li_2WO_4	33.5	560
$Li_2SO_4-K_2SO_4$	Li_2SO_4	860	K_2SO_4	α-Li_2SO_4	12.5	574	β-Li_2SO_4	20.5	535
$K_2WO_4-K_2SO_4$	K_2WO_4	926	K_2SO_4	K_2WO_4	35	916	K_2SO_4	–	–
$Li_2WO_4-K_2SO_4$	Li_2WO_4	738	K_2SO_4	α-Li_2WO_4	13	660	β-Li_2WO_4	30.5	500
$K_2WO_4-Li_2SO_4$	K_2WO_4	926	Li_2SO_4	K_2WO_4	33.5	620	K_2SO_4	43.5	510

All of the data on the compositions are expressed in mole percents.

Binary systems (Table 1, Fig. 2). 1. The system $Li_2WO_4-Li_2SO_4$ was studied first, eutectic at 68% Li_2SO_4 and 596°. From the thermodifferential analysis data the presence of polymorphic transformation at 660° was observed, for lithium tungstate.

2. $K_2WO_4-K_2SO_4$, according to Amadori [2], form continuous solid solutions. The melting point of potassium tungstate, according to Amadori, was taken as 896°, and not 926°; consequently, the study of the system was repeated up to 80% of K_2WO_4. We established that the system is a eutectic with limited solid solutions. Between the values of the ionic radii, equal for SO_4'' to 2.95 A, and for WO_4'' to 3.65 A [5], there exists a difference of 0.7 A, and consequently with a small ionic radius of 0.6 A for lithium in the system $Li_2WO_4-Li_2SO_4$ we have a sharply defined eutectic, as a result of which the concentrations of the reciprocal solid solutions of the components can hardly be especially great.

With increase in the ionic radius of the cation the reciprocal concentration of the solid solutions should increase; consequently, in the system $K_2WO_4-K_2SO_4$ it is postulated that there is a considerably greater tendency for the formation of solid solutions. Both branches of potassium tungstate and potassium sulfate intersect at a shallow angle in the eutectic point of 916° and 35% of K_2SO_4. The K_2WO_4 branch drops from 926° down to a total of only 916° over an extent of 35%, which also indicates the presence of solid solutions of higher concentration.

3. $Li_2WO_4-K_2WO_4$ was studied by Van-Liempt [3]. The compound $Li_2WO_4 \cdot K_2WO_4$ was established in the system, melting at 632°, eutectic points: 572° and 32% K_2WO_4 and 575° and 63.5% K_2WO_4. According to our data, the eutectic points correspond to 560° and 33.5% K_2WO_4 and 575° and 63.5% K_2WO_4, and the compound melts at 626°. On the Li_2WO_4 branch at 660° and 14% of potassium tungstate there is observed a break, characterizing the polymorphic transformation of lithium tungstate.

4. $Li_2SO_4-K_2SO_4$ has been studied more than once. According to the data of E. Nacken [4], the system contains the compound $Li_2SO_4 \cdot K_2SO_4$, melting at 716°, and has eutectic points at 536° and 20% K_2SO_4 and 698° and 60% K_2SO_4. According to our data, the compound melts at 736°,** the eutectic points being: 535° and 20.5% K_2SO_4 and 712° and 60.6% K_2SO_4.

Diagonal sections. Neither of the diagonal sections is stable, and both intersect the fields of the exchange products.

1. $K_2WO_4-Li_2SO_4$ (Table 1, Figs. 1 and 3). The liquidus curve intersects the crystallization fields of potassium tungstate, the β-modification of potassium sulfate, the double sulfate of lithium and potassium, and the α- and β-modifications of lithium sulfate.

2. $Li_2WO_4-K_2SO_4$ (Table 1, Figs. 1 and 3), intersects the crystallization fields of the α- and β-modifications of lithium tungstate, the double sulfate of lithium and potassium, and potassium sulfate.

The transition point of the α- and β-modifications of lithium tungstate lies at 13% K_2SO_4 and 660°.

* Percent of added component.

** The presence of the compound $2Li_2SO_4 \cdot K_2SO_4$ "lithium langbeinite", analogous to $2MgSO_4 \cdot K_2SO_4$, was established by A. G. Bergman and E. K. Akopov; it melts with decomposition at 573°. The appearance of this compound was not confirmed in our investigations, neither was the homeomorphic transformation of this compound in the temperature interval 630-646°.

TABLE 1 (continued)

Branches of crystallization and their intersection points							M.p. of added compo-nent	M.p. of com-pound	Eutectic temperature
branch 3	intersection of 3 and 4		branch 4	intersection of 4 and 5		branch 5			
	%*	t		%*	t				
Li_2SO_4	–	–	–	–	–	–	860°	–	596°
$Li_2WO_4 \cdot K_2WO_4$	63.5	572°	K_2WO_4	–	–	–	926	626°	560; 572
$Li_2SO_4 \cdot K_2SO_4$	60.6	712	K_2SO_4	–	–	–	1069	736	535; 712
–	–	–	–	–	–	–	1069	–	916
$Li_2SO_4 \cdot K_2SO_4$	56.5	576	β-K_2SO_4	57	596°	α-K_2SO_4	1069	–	–
$Li_2SO_4 \cdot K_2SO_4$	81	480	β-Li_2SO_4	91.5	574	α-Li_2SO_4	860	–	–

Ten internal sections were studied to bring out the contour of the crystallization surface of the reciprocal system, the direction of which is shown in Fig. 4, and the form of the curves in Figs. 5, 6 and 7.

The position of the nonvariant points of the system and the lines of mutual crystallization of the components and their compounds are shown in the form of projections of the indicated points and lines of the reciprocal system on the potassium tungstate-potassium sulfate side (Fig. 8) of the diagram; in addition, the polymorphic transformations for lithium tungstate and sulfate are depicted.

In the reciprocal system the presence of nine crystallization fields was established, among which the area of the square was distributed in the following manner: the fields of the components of the α- and β-modifications of K_2SO_4 26.9%, the α- and β-modifications of Li_2WO_4 23.25%, the fields of the $Li_2SO_4 \cdot K_2SO_4$ compounds 21.8%, $Li_2WO_4 \cdot K_2WO_4$ 10.04%, the fields of the components of the α- and β-modifications of Li_2SO_4 5.38%, and K_2WO_4 12.66%. The fields of the complex compounds occupy the greater part of the area of the square. The isotherms, drawn through 50°, clearly outline the contours of the fields, which can clearly be seen in the photograph of the space model (Fig. 9).

There are three eutectic points and one transition point in the system (Figs. 1 and 8). The points, corresponding to 520°, bear the character of inversion points and in their turn (Figs. 4 and 7) are the eutectic

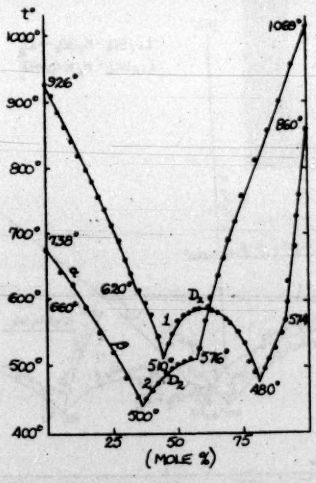


Fig. 3. Diagonal sections. 1) K_2WO_4–Li_2SO_4; 2) $LiWO_4$–K_2SO_4; D_2 – $Li_2SO_4 \cdot K_2SO_4$.

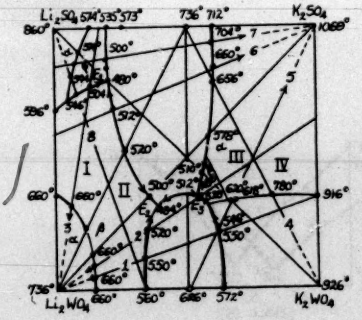


Fig. 4. Index of the internal sections through the reciprocal system Li, K ‖ SO_4, WO_4.

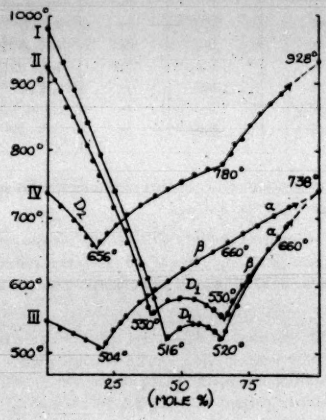


Fig. 5. Internal sections through the system. $D_1 \rightarrow$ $\rightarrow LiWO_4 \cdot K_2WO_4$: $D_2 - Li_2SO_4 \cdot K_2SO_4$.

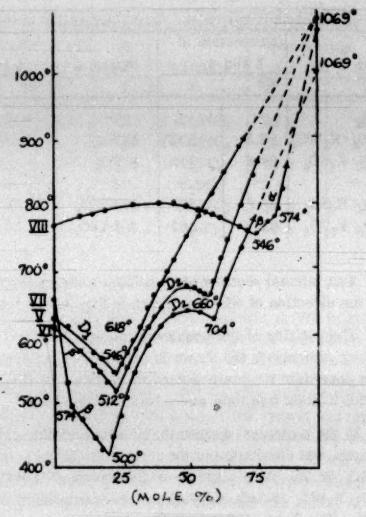


Fig. 6. Internal sections through the system. $D_1 \rightarrow$ $\rightarrow Li_2WO_4 \cdot K_2WO_4$: $D_1 - Li_2SO_4 \cdot K_2SO_4$.

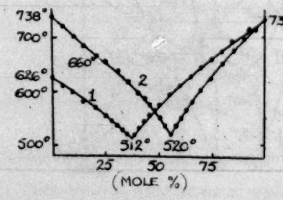


Fig. 7. Stable sections through the system.
1) $Li_2WO_4 \cdot K_2WO_4 - Li_2SO_4 \cdot K_2SO_4$;
2) $Li_2WO_4 - Li_2SO_4 \cdot K_2SO_4$.

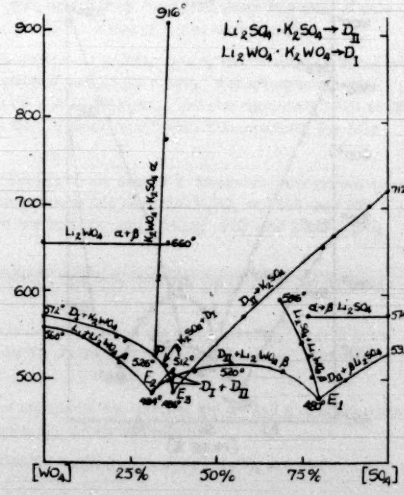
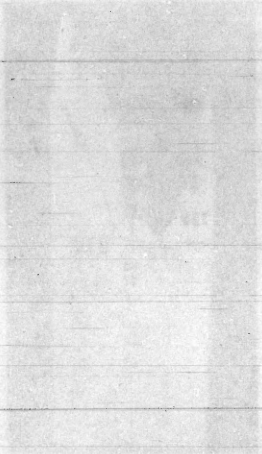


Fig. 8. Projection of the crystallization trees of the reciprocal system on the $K_2WO_4 - K_2SO_4$ side. $D_1 \rightarrow Li_2WO_4 \cdot K_2WO_4$; $D_2 \rightarrow Li_2SO_4 \cdot K_2SO_4$.

Fig. 9. Three-dimensional diagram of the reciprocal system Li, K || SO_4, WO_4.



points of the stable sections, possessing the character of simple binary systems.

The section $Li_2WO_4 \cdot K_2WO_4 - Li_2SO_4 \cdot K_2SO_4$ is the most stable,* since the crystallization fields of the binary compounds appear as quite sharply defined ridges, situated along the given section, although its eutectic temperature of 512° is slightly below the eutectic temperature of 520° for the stable section proceeding from the zone of the double sulfate of lithium and potassium and directed toward the lithium tungstate.

In Fig. 10 is shown the diagram for the crystallization trees of the system.

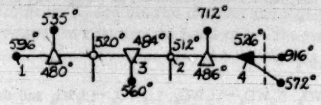


Fig. 10. Scheme for the crystallization trees of the reciprocal system. 1) Eutectic points of the binary system; 2) inversion points; 3) ternary eutectic points; 4) ternary transition point.

The absence of data on the heats of formation of Li_2WO_4, K_2WO_4 and of the compounds formed by them does not permit calculating the conditional thermochemical effect of the exchange reaction. It must be assumed that it is extremely slight, as can be determined from the fusion diagram. The heat of formation of $Li_2SO_4 \cdot K_2SO_4$ was determined in the study [6].

The reaction between the components of the system proceeds, in accord with the equations, in the direction of forming both of the double salts $Li_2SO_4 \cdot K_2SO_4$ and $Li_2WO_4 \cdot K_2WO_4$:

$$2Li_2SO_4 + 2K_2WO_4 \rightarrow Li_2SO_4 \cdot K_2SO_4 + Li_2WO_4 \cdot K_2WO_4,$$

$$2Li_2WO_4 + 2K_2SO_4 \rightarrow Li_2SO_4 \cdot K_2SO_4 + Li_2WO_4 \cdot K_2WO_4.$$

The zone cross section $Li_2SO_4 \cdot K_2SO_4 - Li_2WO_4 \cdot K_2WO_4$ (Fig. 4) divides the composition square into two tetragons, each of which in turn is subjected to a secondary triangulation of the sections, obtained as the result of the reactions proceeding in the tetragons between the components and the compounds:

$$Li_2SO_4 \cdot K_2SO_4 + 2K_2WO_4 \rightarrow Li_2WO_4 \cdot K_2WO_4 + 2K_2SO_4,$$

$$Li_2WO_4 \cdot K_2WO_4 + 2Li_2SO_4 \rightarrow Li_2SO_4 \cdot K_2SO_4 + 2Li_2WO_4.$$

The first tetragon $Li_2SO_4 - Li_2SO_4 \cdot K_2SO_4 - Li_2WO_4 \cdot K_2WO_4 - Li_2WO_4$ is divided by the second stable section $Li_2SO_4 \cdot K_2SO_4 - Li_2WO_4$ into two phase triangles:**

(I) $Li_2WO_4 - Li_2SO_4 - Li_2SO_4 \cdot K_2SO_4$

and

(II) $Li_2WO_4 - Li_2SO_4 \cdot K_2SO_4 - Li_2WO_4 \cdot K_2WO_4$,

with eutectic points E_1 = 480° and E_2 = 484° (Fig. 4).

TABLE 2

Compositions and Temperatures of the Nonvariant Points

Designation of point	Character of point	Temperature	Composition (in mole %)				Equilibrium phases
			Li_2WO_4	K_2SO_4	K_2WO_4	Li_2SO_4	
E_1	Eutectic	480°	20	20	–	60	β-Li_2SO_4; $Li_2SO_4 \cdot K_2SO_4$; β-Li_2WO_4
E_2		484	30	–	37.5	32.5	β-Li_2WO_4; $Li_2SO_4 \cdot K_2SO_4$; $Li_2WO_4 \cdot K_2WO_4$
E_3		486	47	37.5	15.5	–	β-K_2SO_4; $Li_2WO_4 \cdot K_2WO_4$; $Li_2SO_4 \cdot K_2SO_4$
P	Transition	526	42	37.5	20.5	2	$Li_2WO_4 \cdot K_2WO_4$; K_2WO_4; β-K_2SO_4

The second tetragon $Li_2WO_4 \cdot K_2WO_4 - Li_2SO_4 \cdot K_2SO_4 - K_2SO_4 - K_2WO_4$ is also subjected to triangulation into two phase triangles by the section $Li_2WO_4 \cdot K_2WO_4 - K_2SO_4$, not possessing the character of a eutectic system. The melts, entering into the third phase triangle $Li_2WO_4 \cdot K_2WO_4 - K_2SO_4 \cdot Li_2SO_4 - K_2SO_4$, completely solidify at the point E_3 at 486°. The melts of the fourth phase triangle solidify at the ternary transition point P at 526°.

* In Fig. 1 the stable sections are designated by a solid line, the unstable sections by a dotted line.

** In Fig. 4 the phase triangles of both tetragons are designated by Roman numerals.

The compositions of the nonvariant points of the system and of their corresponding equilibrium phases are given in Table 2.

In accord with the classification of Bergman and Bukhalova, the depicted system belongs to the type of adiagonal-belt systems. Apparently, such systems will always be observed in those cases where the free energy of formation of the compounds (or approximately the heat effect for compound formation) is greater than the corresponding value for the exchange decomposition reaction.

The system Li, K || SO_4, MoO_4 [7] studied by us has a similar character. Apparently, the effective radii of their anions, calculated as being fairly close values, make for similar fusion diagrams. Even the area sum of the fields of the compounds in the two systems is of the same order: 31.84% for the system Li, K || SO_4, WO_4 and 30.15% for Li, K || SO_4, MoO_4.

SUMMARY

1. The liquidus curves of the binary systems: K_2SO_4–K_2WO_4, K_2WO_4–Li_2WO_4, Li_2WO_4–Li_2SO_4 and the surface of crystallization of the reciprocal system Li, K || SO_4, WO_4 were studied by the visual-polythermal fusion method.

2. The system in its character belongs to the class of adiagonal-belt systems of the eutectic type.

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* See Consultants Bureau Translation, page 2171.

RECIPROCAL SYSTEM OF SILVER AND SODIUM IODIDES AND NITRATES

M. A. Zakharchenko and A. G. Bergman

The ternary reciprocal system Ag, Na ‖ I, NO_3 is the concluding system of the series of reciprocal systems of halides (Cl, Br and I) and nitrates of silver and sodium studied by us, which are of interest for the theory of reciprocal systems and the chemistry of fused salts. The system of silver and sodium iodides and nitrates studied by us demonstrates an extremely clear case of a sharply singular system with stratification (Fig. 1).

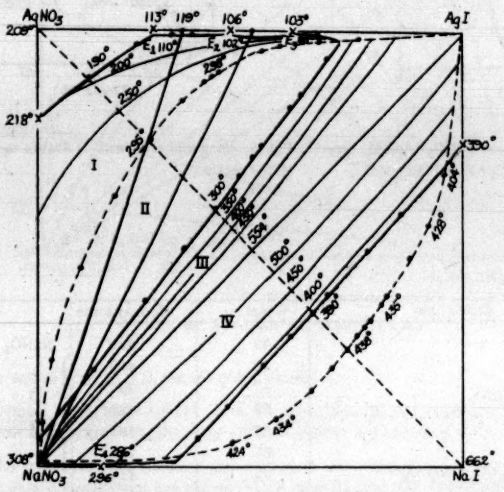

Fig. 1. Liquidus diagram of the reciprocal system.

EXPERIMENTAL

The study was made by the visual-polythermal method using a nichrome-constantan thermocouple in a high-melting glass test tube fitted with coupling. The calculations are expressed in mole percent. The starting substances were C.P. $AgNO_3$, $NaNO_3$, NaI, twice recrystallized. Silver iodide was prepared by its precipitation from a solution of C.P. silver nitrate with potassium iodide.

TABLE 1

System AgI—NaI

% NaI	temperature	% NaI	temperature	% NaI	temperature	% NaI	temperature
0	554°	25	390°	45	472°	70	562°
5	524	27	399	50	490	75	580
10	492	30	412	55	509	80	596
15	460	35	432	60	527	90	630
20	424	40	452	65	544	100	662

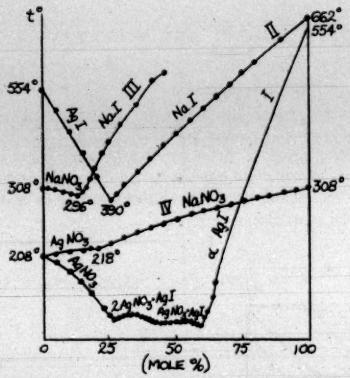

Fig. 2. Binary systems. I) System $AgNO_3$–AgI; II) system AgI–NaI; III) system $NaNO_3$–NaI; IV) system $AgNO_3$–$NaNO_3$.

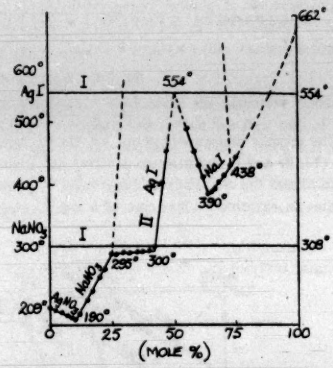

Fig. 3. Diagonal sections. I) Stable section; II) metastable section.

TABLE 2

Metastable Diagonal Section $AgNO_3$–NaI

% NaI	Temperature	Solid phase	% NaI	Temperature	Solid phase
0	209°		42	300°	$NaNO_3$ + AgI
2	205		45	408	
5	201		47	460	
7	197	$AgNO_3$	55	497	
9	194		58	460	AgI
10	192		60	438	
11	S* 190	$AgNO_3$ + $NaNO_3$	62	418	
12	198		64	392	
17	234		65	390	AgI + NaI
20	257		66	398	
22	269		68	409	
25	295		70	419	NaI
27	295.5	$NaNO_3$	73	438	
30	296		75	450	
32	296.5				
35	297				
37	298				
40	299				

Remarks: Stratification from 25% NaI and 295° to 73% NaI and 438°.

The determination of the incipient crystallization temperatures was strongly hindered due to the intense color of the silver iodide and, consequently, almost complete opaqueness of some of the melts. However, illumination with a strong light beam made it possible to detect the beginning of crystallization quite accurately. Examination of the melt and of the first crystals through a magnifying glass even makes it possible to visually detect the appearance of a new solid phase, and also to more exactly differentiate the beginning of stratification from the beginning

* S is the intersection point of the liquidus branches, found graphically.

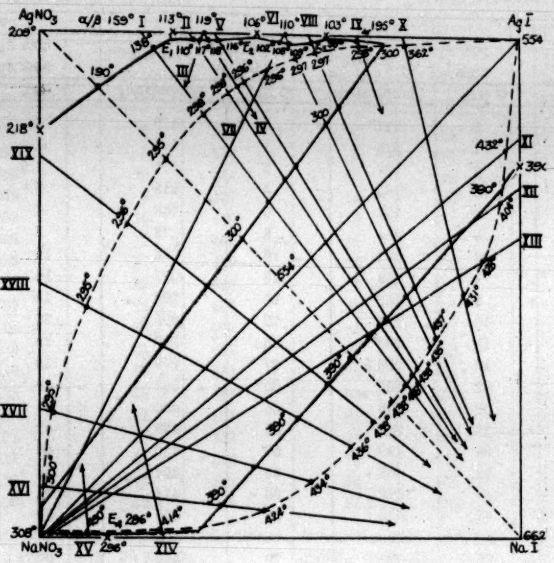

Fig. 4. Direction of internal sections.

of crystallization and to observe it in the stratification region.

Binary systems. 1. $AgNO_3$–AgI [1]. N. S. Dombrovskaya [2] established the presence of two compounds, melting without decomposition: $2AgNO_3 \cdot AgI$ 119° and $AgNO_3 \cdot AgI$ 109° (Fig. 2, I).

2. AgI–NaI – limited solid solutions with a eutectic, according to our determinations, at 390° and 75% AgI. According to the data of Sandonnini and Skarpa [3] the eutectic is at 390° and 65.5% AgI (Table 1, Fig. 2, II).

3. $NaNO_3$–NaI [4]. Eutectic at 296° and 14% NaI (Fig. 2, III).

4. $AgNO_3$–$NaNO_3$ [5, 6]. Solid solutions with peritectic at 217.5° and 80% $AgNO_3$ (Fig. 2, IV).

Diagonal sections. 1. The stable diagonal section AgI–$NaNO_3$ is characterized by complete lack of solubility of the components in the liquid state; its phase diagram is represented as two straight horizontal lines, corresponding to the melting points of silver iodide 554° and sodium nitrate 308° (Fig. 3, I).

2. The metastable diagonal section $AgNO_3$–NaI intersects the crystallization fields of silver nitrate, sodium nitrate, silver iodide and sodium iodide. The diagram of the metastable pair $AgNO_3$–NaI is characterized by a clearly expressed singularity at an ordinate of 50%, which is noted in the intersection at a sharp angle of the crystallization branches of the silver iodide reaction product (Table 2, Fig. 3, II).

In the interval from 47 to 55% NaI the crystallization curve for silver iodide, depicted on the diagram of the metastable section by a dotted line, was extrapolated due to the decomposition of the salts.*

For this reason we were unable to determine the upper limit of the stratification region; the stratification curves rise upward almost vertically: the critical point fails to be found at extremely high temperatures.**

* This also relates to all of the other sections passing through a singular maximum.

** The binodal curve on the diagrams of the metastable diagonal and all of the internal sections is shown by a dotted line.

TABLE 3

Internal Sections of the Reciprocal System

I		II		V		VI	
80% $AgNO_3$ 20% AgI → NaI		70% $AgNO_3$ 30% AgI → NaI		65% $AgNO_3$ 35% AgI → NaI		50% $AgNO_3$ 50% AgI → NaI	
% NaI	temperature	% NaI	temperature	% NaI	temperature	% NaI	temperature
0	142°	0	117°	0	119°	0	110°
2	140	1	115	1	116	1	109.5
4	157	2	137	2	170	1.5	109
6	190	3	160	4	215	2	215
8	216	4	184	6	248	4	297
10	237	5	204	8	279	8	298
12	269	6	221	10	296	10	298.5
15	295	7	239	15	297	14	299
16	298	8	252	20	298	18	300
20	298.5	10	274	22	298.5	20	331
24	299	12	298	25	299	25	419
30	299.5	18	298.5	27	299.5	30	510
35	336	22	299	30	347	40	496
40	460	30	300	35	450	45	445
50	596	32	341	45	505	47	423
55	439	35	419	50	450	48	417
59	400	45	508	55	404	50	403
62	396	49	472	60	414	51	394
63	402	55	416	62	425	53	396
65	413	57	396	65	439	55	404
70	438	65	427	70	460	60	424
75	480	70	440	75	482	62	435

Intersection points: 138°, 3% NaI; 300°, 34% NaI; 390°, 60.5% NaI. Stratification from 18% NaI and 298° to 70% NaI and 438°

Intersection points: 115°, 1% NaI; 300°, 30% NaI; 390°, 58% NaI. Stratification from 12% NaI and 298° to 68% NaI and 438°

Intersection points: 116°, 1% NaI; 300°, 28% NaI; 390°, 57% NaI. Stratification from 10% NaI and 296° to 65% NaI and 439°.

Intersection points: 109°, 1.5% NaI; 300°, 18% NaI; 390°, 51.5% NaI. Stratification from 4% NaI and 297° to 62% NaI and 435°.

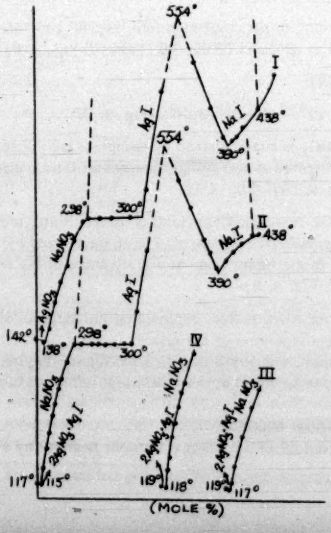

Fig. 5. Internal sections. I) 80% $AgNO_3$ + + 20% AgI → NaI; II) 70% $AgNO_3$ + 30% AgI → NaI; III) 67% $AgNO_3$ + 33% AgI → → $NaNO_3$; IV) 67% $AgNO_3$ + 33% AgI → → NaI.

TABLE 4

Internal Sections of the Reciprocal System

X		XI		XIII		XVIII	
25% $AgNO_3$ / 75% AgI → NaI		80% AgI / 20% NaI → $NaNO_3$		60% AgI / 40% NaI → $NaNO_3$		50% $AgNO_3$ / 50% $NaNO_3$ → NaI	
% NaI	temperature	% $NaNO_3$	temperature	% $NaNO_3$	temperature	% NaI	temperature
0	337°	0	424°	0	452°	0	262°
1	352	2	429	5	437	5	278
2	362	5	434	10	423	8	290
3	378	8	437	13	416	15	296
4	388	10	440	16	412	20	299
5	398	15	446	21	402	25	300
8	435	17	450	25	396	26.5	352
10	456	20	455	29	390	30	461
12	480	26.5	466	35	401	38.5	507
27	494	28.5	468	41	415	42	477
30	470	34	476	44	422	45.5	447
33	449	39	481	50	438	50	404
36	423	45	487	55	450	51	394
40	394	51	494	60	461	55	402
45	407	55	499	70	485	60	422
48	417	65	512	75	497	64	436
51	431	75	528	82	507	70	476
53	439	82.5	548	85.5	512	75	508
Intersection point: 390°, 41% NaI. Stratification from 2% NaI and 362° to 51% NaI and 431°.		Beginning of stratification 432°, 3% $NaNO_3$.		Intersection point: 390°, 30% $NaNO_3$. Beginning of stratification: 428°, 8% $NaNO_3$.		Intersection points: 300°, 25% NaI; 390°, 52% NaI. Stratification from 9% NaI and 295° to 64% NaI and 436°	

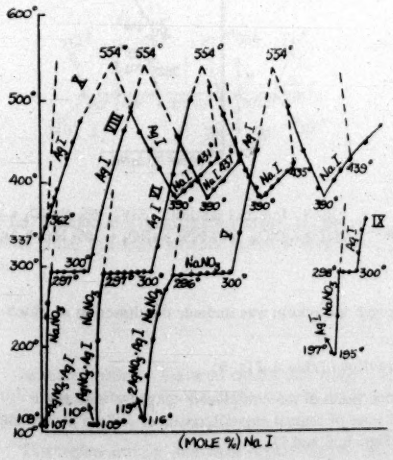

Fig. 6. Internal sections. V) 65% $AgNO_3$ + 35% AgI — NaI; VI) 50% $AgNO_3$ + 50% AgI — NaI; VIII) 45% $AgNO_3$ + 55% AgI — NaI; IX) 35% $AgNO_3$ + 65% AgI — NaI; X) 25% $AgNO_3$ + + 75% AgI — NaI.

TABLE 5

Areas of the Crystallization Fields of the Salts in the System

Designation No.	Crystallization fields	In percent of the area of the projection of the reciprocal system liquidus
1	$AgNO_3$	2.9
2	$2AgNO_3 \cdot AgI$	0.2
3	$AgNO_3 \cdot AgI$	0.2
4	$NaNO_3$	31.7
5	AgI	39.9
6	NaI	25.1

The study is possible up to 75% NaI and 450°; further addition of sodium iodide evokes the decomposition of the nitrates, consequently, part of the curve for the separation of NaI crystals, indicated in Fig. 3, II, by a dotted line, is plotted by extrapolation.

TABLE 6

Crystallization Temperatures and Compositions of the Multiple Points

Phase triangle	Apexes of the phase triangle	Character of the point	Temperature of the ternary point	Composition of the ternary point (%)
I	$2AgNO_3 \cdot AgI$, $AgNO_3$, $NaNO_3$	Eutectic	110°	73.0 $AgNO_3$ 1.0 $NaNO_3$ 26.0 AgI
II	$2AgNO_3 \cdot AgI$, $AgNO_3 \cdot AgI$, $NaNO_3$	Eutectic	102	55.0 $AgNO_3$ 1.5 $NaNO_3$ 43.5 AgI
III	$AgNO_3 \cdot AgI$, AgI, $NaNO_3$	Eutectic	98	40.25 $AgNO_3$ 0.75 $NaNO_3$ 59.0 AgI
IV	AgI, $NaNO_3$, NaI	Eutectic	286	85.5 $NaNO_3$ 0.5 AgI 14.0 NaI

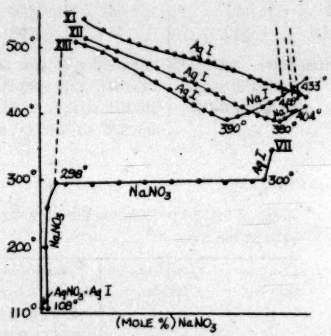

Fig. 7. Internal sections. XI) 80% AgI + 20% NaI → $NaNO_3$; XII) 70% AgI + 30% NaI → $NaNO_3$; XIII) 60% AgI + 40% NaI → → $NaNO_3$; VII) 50% $AgNO_3$ + 50% AgI → $NaNO_3$.

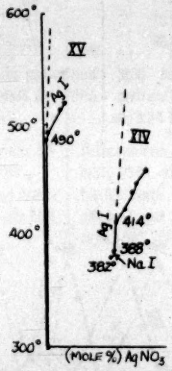

Fig. 8. Internal sections. XIV) 75% $NaNO_3$ + 25% NaI → $AgNO_3$; XV) 90% $NaNO_3$ + 10% NaI → $AgNO_3$.

Internal sections. A total of 19 internal sections* through the system was studied, the direction of which can be seen from Fig. 4.

Section I in character resembles an unstable diagonal section (Table 3, Fig. 5).

Sections II-VIII completely determine the crystallization fields of the complexes: $2AgNO_3 \cdot AgI$ and $AgNO_3 \cdot AgI$, and also in part, the region of stratification and lines of mutual crystallization of sodium nitrate and silver iodide, and sodium iodide and silver iodide (Table 3, Figs. 5, 6 and 7).

* All of the points, obtained experimentally, are plotted on the diagrams of the internal sections, while in the tables for the sake of brevity the same series of points as in the sections are omitted.

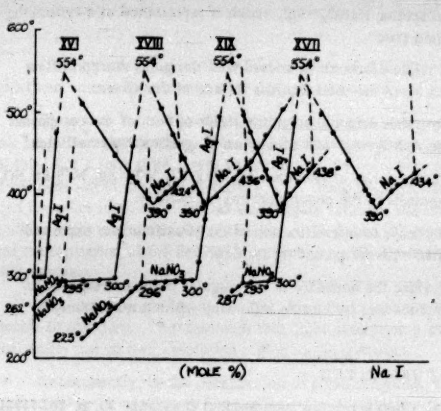

Fig. 9. Internal sections. XVI) 90% $NaNO_3$ + 10% $AgNO_3$ → → NaI; XVII) 75% $NaNO_3$ + 25% $AgNO_3$ → NaI; XVIII) 50% $NaNO_3$ + 50% $AgNO_3$ → NaI; XIX) 25% $NaNO_3$ + 75% $AgNO_3$ → → NaI.

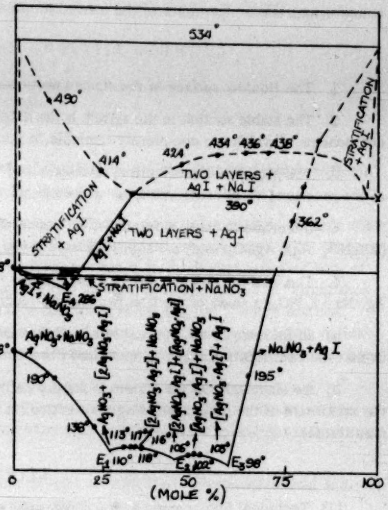

Fig. 10. Projection of mutual crystallization lines and stratification lenses on the $NaNO_3$–NaI side.

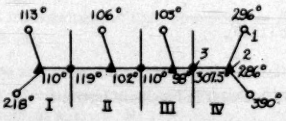

Fig. 11. Scheme of crystallization trees. 1) Binary eutectic point; 2) ternary eutectic point; 3) inversion point.

Sections IX-XIII delineate the region of stratification on the AgI–NaI side and together with this the curve for the mutual crystallization of silver iodide and sodium iodide (Table 4, Figs. 6 and 7).

Sections XIV-XIX determine the region of stratification and the crystallization fields of sodium nitrate, silver iodide and sodium iodide in the triangle $NaNO_3$– –$AgNO_3$–NaI (Table 4, Figs. 8 and 9).

Surface of the Liquidus

The combination of the given binary systems, the diagonal sections and the internal sections made it possible fully to establish the character of the liquidus surface of the reciprocal system, consisting of six crystallization fields, the dimensions of which are given in Table 5.

In accord with the elevated conditional thermal effect of the exchange reaction (28.38 kcal), the region of stratification situated along the stable diagonal, is extremely broad and occupies 64.3% of the total surface area of the system.

This region extends into three crystallization fields, covering the greater part of the sodium nitrate field, nearly all of the silver iodide field and part of the sodium iodide field.

The peculiar characteristic of the given reciprocal system is the enormous ridge, situated along the stable diagonal. It exerts a deformative effect on the crystallization fields of both compounds, as a result of which these fields prove to be tightly squeezed to one side.

In Fig. 10 is given the projection of the mutual crystallization lines and the stratification lenses on the $NaNO_3$–NaI side.

The indicated character of the system can be expressed by the scheme of crystallization trees (Fig. 11). The compositions and temperatures of the nonvariant points in the system are given in Table 6.

SUMMARY

1. The liquidus surface of the studied reciprocal system consists of six crystallization fields.

2. The stable section in the system is the diagonal section $NaNO_3$–AgI, which is represented as a system, the components of which are completely insoluble in the liquid state.

3. The region of stratification, situated along the stable diagonal, in accord with the great thermal effect of the reaction (28.38 kcal), occupies an area equal to 64.3% of the total liquidus surface of the system.

4. Under the strongly deformative influence of the stable diagonal ridge the fields of both of the compounds ($2AgNO_3 \cdot AgI$, $AgNO_3 \cdot AgI$) are tightly pressed to the side $AgNO_3$–AgI and occupy an insignificantly small area.

5. The system is completed by a study of the following series of systems: Ag, Na ‖ Cl, NO_3; Ag, Na ‖ Br, NO_3; Ag, Na ‖ I, NO_3; a study of the first two systems lends exactness to the conclusions made, namely:

a) an increase in the thermal effect of the reaction leads to intensification of the stratification, expressed in that the stratification region is increased when compared with the preceding systems;

b) the singularity of the system is sharply defined, since the boundary of the singular plane corresponds to the maximum of the metastable diagonal section (in the preceding systems an inflection without maximum was manifested).

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STUDY OF THE SYSTEM $Co(ClO_4)_2 - Li_2Br_2 - (H_2O)$ - METHYL ETHYL KETONE BY PHYSICO-CHEMICAL ANALYSIS METHODS

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Contemporary studies show that solutions of salts, especially of multivalent metals, contain together with the usual ions and undissociated molecules, ionic formations of different degree of complexity.

Up to now the composition of the latter could be expressed only by opinions, since there were no reliable methods for their determination. The well known thiocyanate reaction for the trivalent iron ion can serve as an example of this. For a long time it was believed that the color base in the given reaction is ferric thiocyanate $Fe(CNS)_3$ or a complex ion of the type $[Fe(CNS)_6]^{---}$. Using the light absorption study method, Bent and French [1] established that the color of aqueous ferrous thiocyanate solutions was due to the formation of the $FeCNS^{++}$ ion in solution. This reaction was more fully studied by A. K. Babko [2], who on the basis of light absorption measurements indicated the formation of the $FeCNS^{++}$ ion in solution and studied the conditions for the existence of other forms of iron thiocyanate.

The experimental study of light absorption has shown that it is extremely sensitive to the formation of compounds in solutions. Together with this, light absorption is also an extremely selective property, since every chemical entity has its own absorption region in the spectrum.

Consequently, in the construction of phase diagrams, the use of light absorption as a physicochemical analysis method makes it possible to have still another coordinate – the wave length of light.

The data obtained when light absorption is used as a physicochemical method of analysis, taking into consideration the wave length of the light used, can offer great possibilities for the familiarization of systems. The last circumstance was first considered by Ostromyslensky [3], who studied the change in the light absorption of the system nitrobenzene–aniline as a function of composition, and who determined the composition of the nitrobenzene–aniline compound that is stable only in solution.

The measurement of light absorption for studying the composition of compounds formed in solutions was also used by Job [4].

Some studies in this direction have recently appeared in the literature in which light absorption has been studied separately from the other properties of the system, despite the basic precepts laid down by the founder of physicochemical analysis, N. S. Kurnakov, that not one of the physical properties of the system should be studied isolated from the others.

One of the most essential features of physicochemical analysis is the ability simultaneously to study several properties of the system within wide limits of both concentration and temperature changes [5].

The systematic use of light absorption measurement as a physicochemical analysis method is to be found in the work of I. V. Tananaev [6], who developed the physicochemical analysis method for systems possessing great significance in analytical chemistry.

The purpose of the present work is to study the formation of compound in solutions with the aid of light absorption measurements. In this connection the light absorption was studied in conjunction with the other properties of the system (electrical conductivity, viscosity and density), taking into consideration changes in the equilibrium factors (changes in the total concentration of salts and temperature) and the interaction of all of the components in the system.

In the present paper are given the results of studying the system $Co(ClO_4)_2 - Li_2Br_2 - (H_2O)$ – methyl ethyl ketone, which, as far as we know, is not described in the literature.

EXPERIMENTAL

Preparation of the substances and solutions. Methods of study. Cobalt perchlorate $Co(ClO_4)_2 \cdot 6H_2O$ was prepared from cobalt carbonate (C.p.) and perchloric acid (very pure) [7]. Prior to the preparation of solutions the

compound was recrystallized twice. In the recrystallization a temperature not exceeding 50° was used in the evaporation of the solution. Heating at higher temperatures is accompanied by hydrolysis of the salt, producing a slight turbidity in concentrated aqueous solutions. We were unable to obtain the anhydrous cobalt perchlorate. Decomposition was observed when we tried to prepare it by the dehydration of the hexahydrate $Co(ClO_4)_2 \cdot 6H_2O$ (in vacuo with heating).

Cobalt bromide $CoBr_2 \cdot 6H_2O$ was obtained from cobalt carbonate and hydrobromic acid (C.p.) with subsequent recrystallization.

Lithium bromide $LiBr \cdot H_2O$ was obtained from lithium carbonate (C.p.) and hydrobromic acid (C.p.), and after two recrystallizations was dried at 100° [8]. Lithium perchlorate $LiClO_4 \cdot 3H_2O$ was obtained by dissolving lithium carbonate (C.p.) in perchloric acid. The twice recrystallized $LiClO_4 \cdot 3H_2O$ was dried at 70° [9]. The methyl ethyl ketone was dehydrated over fused potash and distilled twice, collecting the distillate fraction with b.p. 73.6°. The presence of water in the system was determined by its amount in the hexahydrate $Co(ClO_4)_2 \cdot 6H_2O$.

The amount of solvent, necessary for preparing the solutions, and also mixtures of solutions, was measured by the volume calculated from the density prevailing at the volume calibration temperature. On the average the volume of mixed solutions was 50 ml and it was measured in a buret graduated to 0.1 ml. The solutions were always freshly prepared. The solution concentrations were always expressed in mole percents.

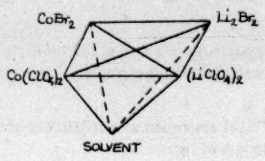

Fig. 1. System $Co(ClO_4)_2$–$CoBr_2$–Li_2Br_2–$(LiClO_4)_2$–solvent.

The absorption of monochromatic light by the solutions was measured on an SF-11 photoelectric spectrophotometer, making it possible to measure the absorption spectra in the wave length region of 220 to 1100 mμ with an average error of less than 1%. To prevent the influence of temperature changes on the accuracy of the instrument the cuvettes were placed in a closed ebonite carriage with glass windows. Water was used to maintain the desired temperature in the ultrathermostat; with the aid of a small turbine, the water was circulated through the metal jacket heads screwed on the mounting of the round cuvettes. The cuvettes, used for measuring the optical density of the solutions at elevated temperatures, were glass rings, closed at the ends with round glass windows. The depth of the solution layer was made equal to the thickness of the ring. The optical density of the solutions was measured in the spectrum region 600-740 mμ in intervals of 5 mμ.

In the present paper are given the optical density-composition isotherms at the wave lengths where the singular points appear most distinctly.

The apparatus for measuring the electrical conductivity consisted of a resistance bridge and a sound generator with amplifier for supplying the bridge and indicator, consisting of a two-cascade band amplifier and built-in indicator.

The densities and viscosities of the solutions were measured by the procedures given in the literature [10]. The densities of the solutions were used to calculate the viscosity values.

Geometric Representation of the Equilibria

The formation of cobaltous bromide complexes in the solutions $Co(ClO_4)_2 + Li_2Br_2 \rightleftharpoons CoBr_2 + 2LiClO_4$ can be represented by a regular pyramid with a square base, at the corners of which are located the salts $Co(ClO_4)_2$. $CoBr_2$, Li_2Br_2 and $(LiClO_4)_2$ and at the apex of which the solvent is located (Fig. 1). Such a pyramid, bound by four equilateral triangles, represents half of a regular octahedron. The possible combinations of salts, participating in the reactions of this system, consist of the pairs:

$CoBr_2$–Li_2Br_2
$CoBr_2$–$Co(ClO_4)_2$
$LiClO_4$–$LiBr$
$Co(ClO_4)_2$–$(LiClO_4)_2$
} Side systems, corresponding to the sides of the square.

$Co(ClO_4)_2$–Li_2Br_2
$CoBr_2$–$(LiClO_4)_2$
} Diagonal systems, corresponding to the diagonals of the square.

The solutions of the individual salts are correspondingly represented by four ribs.

The systems $Co(ClO_4)_2-Li_2Br_2-$solvent, $CoBr_2-(LiClO_4)_2-$solvent, in which exchange reactions are possible, belong to the class of quaternary reciprocal systems. The inner space of the pyramid belongs to them, in which in successive order are arranged the solutions of the salts: $Co(ClO_4)_2$, LiBr, $CoBr_2$, $LiClO_4$ and solvent.

The ternary systems: $CoBr_2-Li_2Br_2-$solvent, $CoBr_2-Co(ClO_4)_2-$solvent, $LiBr-LiClO_4-$solvent, $Co(ClO_4)_2-(LiClO_4)_2-$solvent, are situated on the planes of the side boundaries.

System $Co(ClO_4)_2 - Li_2Br_2 - (H_2O)$ – Methyl Ethyl Ketone

Total salts 0.12 mole %, (H_2O 0.72 mole %), methyl ethyl ketone 99.16 mole %.

In the investigated portion of the spectrum the lithium bromide solution, as well as the cobalt perchlorate solution, at a layer thickness of 1 mm, fails to absorb light. The absorption observed for the system in the 600-720 mμ region of the spectrum is due to the formation of cobaltous bromide compounds. To determine their composition, together with the light absorption, both their electrical conductivity and viscosity were measured.

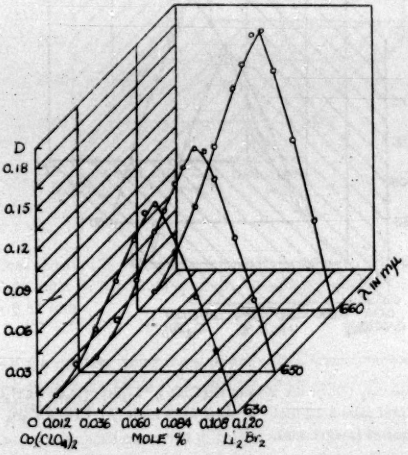

Fig. 2. Optical density (D) of the system $Co(ClO_4)_2-Li_2Br_2-(H_2O)-CH_3COC_2H_5$. Total salts 0.12 mole % (H_2O 0.72 mole %), $CH_3COC_2H_5$ 99.16 mole %. Thickness of layer 1 mm.

In Fig. 2 are shown the optical density isotherms at wave lengths of 630, 650 and 660 mμ. The optical density isotherm at 630 mμ consists of two branches, intersecting in the maximum, the abscissa of which corresponds to the ratio between $Co(ClO_4)_2$ and Li_2Br_2 of 2:3, which indicates the formation of the compound $CoBr_2 \cdot Li_2Br_2$* in the system. In the 600-650 mμ region of the spectrum the abscissa of this maximum remains constant with change in the wave length of the monochromatic light used in making the light absorption measurements of the system.

The optical density isotherm at 650 mμ (Fig. 2) also consists of two branches, intersecting in the maximum, corresponding to the formation of the compound $CoBr_2 \cdot LiBr$.

* See below. The formation of this compound can be represented by the equation $2Co(ClO_4)_2 + 3Li_2Br_2 = 2(CoBr_2 \cdot LiBr) + 4LiClO_4$.

The optical density isotherm at 660 mμ consists of two branches, intersecting in the maximum, the abscissa (composition) of which corresponds to the ratio between $Co(ClO_4)_2$ and Li_2Br_2 of 1:2, indicating the formation of the compound $CoBr_2 \cdot 2LiBr$ in the system (Fig. 2).

In the 660-720 mμ region of the spectrum the abscissa of this maximum remains constant independent of the change in wave length.

In order to determine if the locations of the singular points found on the optical density isotherms would change with change in the equilibrium factors, we also studied the light absorption in the system of the section with 0.12 mole% of total salts at 20 and 50°, and the section with 0.24 mole % of total salts at room temperature (about 20°).

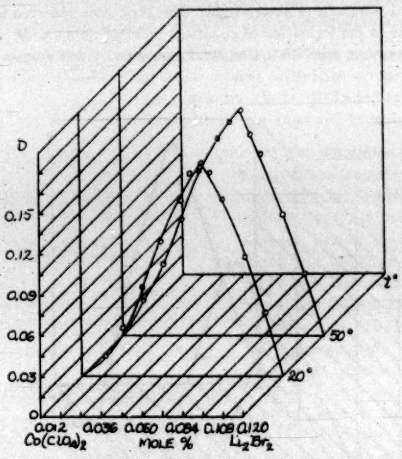

Fig. 3. Optical density (D) of the system $Co(ClO_4)_2-Li_2Br_2-(H_2O)-CH_3COC_2H_5$ at λ 630 mμ. Total salts 0.12 mole %, (H_2O 0.72 mole %), $CH_3COC_2H_5$ 99.16 mole %. Thickness of layer 1 mm.

The optical density isotherms at 630 mμ and 20 and 50° are shown in Fig. 3. The optical density isotherm at 50°, the same as the one at 20°, consists of two branches, intersecting in the maximum, the abscissa (composition) of which corresponds to the ratio between $Co(ClO_4)_2$ and Li_2Br_2 of 2:3, which indicates the formation of the compound $CoBr_2 \cdot LiBr$ in the system.

A comparison of the optical density values of the section with 0.12 mole % of total salts, measured at 20 and 50° (Fig. 3), shows that elevation of the temperature from 20 to 50° is accompanied by an increase in the optical density, however, here the abscissa (composition) of the singular points on the optical density isotherms remains constant.

The optical density isotherms at 635 and 680 mμ for the system with 0.24 mole % of total salts are shown in Fig. 4. With increase in the total amount of salts in the given system the light absorption increases. The singular points, found on the optical density isotherms of the section with 0.12 mole % of total salts, are confirmed on the optical density isotherms with double the amount of salts. The shifting of the optical density isotherms, on which the singular points are more clearly defined for the section with 0.24 mole % of total salts, in the direction of the longer wave lengths is explained by the decreased solvation of the cobaltous bromide complexes, occurring as the result of increase in the total amount of salts in the system.

Consequently, with change in the equilibrium factors (concentration of salts and temperature) the abscissa (compositions) of the singular points found on the optical density isotherms of the system $Co(ClO_4)_2-Li_2Br_2-H_2O-$ –methyl ethyl ketone remain constant.

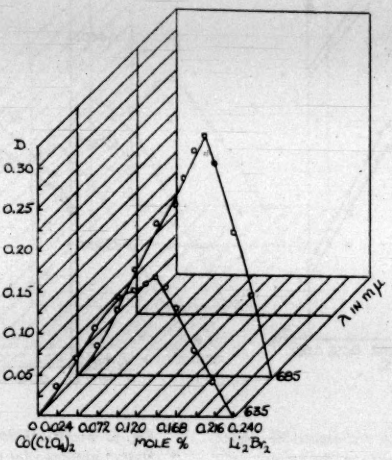

Fig. 4. Optical density (D) of the system $Co(ClO_4)_2-Li_2Br_2-(H_2O)-CH_3COC_2H_5$. Total salts 0.24 mole %, (H_2O 1.44 mole %), $CH_3COC_2H_5$ 98.32 mole %. Thickness of layer 0.52 mm.

In order to determine if the singular points found on the optical density isotherms would appear on the isotherms of other properties, we studied the viscosity (η) and the electrical conductivity (κ) of the given system with 0.12 and 0.24 mole % of total salts.

The κ-composition and $\kappa\eta$-composition curves at 25 and 50° for the system with 0.12 mole % of total salts are shown in Fig. 5. Each of the κ-composition and $\kappa\eta$-composition curves consists of two branches, intersecting in the maximum, the abscissa of which corresponds to the ratio between $Co(ClO_4)_2$ and Li_2Br_2 of 2:3, which indicates the formation of the compound $CoBr_2 \cdot LiBr$ in the system. With increase in the temperature from 25 to 50° the abscissa (composition) of the maximum remains constant.

The results of the electrical conductivity and electrical conductivity corrected for viscosity measurements for the investigated system with 0.24 mole% of total salts are shown graphically in Fig. 6.

Each of the κ-composition and $\kappa\eta$-composition curves (Fig. 6) consists of two branches, intersecting in the maximum, the abscissa of which corresponds to the ratio between $Co(ClO_4)_2$ and Li_2Br_2 of 2:3, which indicates the formation of the compound $CoBr_2 \cdot LiBr$.

With increase in the temperature from 25 to 50° the abscissa of the maximum remains constant. Consequently, a singular point is found on the κ-composition and $\kappa\eta$-composition curves, corresponding to the formation of the compound $CoBr_2 \cdot LiBr$ in the system.

With change in the equilibrium factors (temperature and concentration of salts) the abscissa (composition) of this singular point remains constant.

A comparison of the electrical conductivity values for the systems with 0.12 and 0.24 mole % of total salts reveals that with increase in the concentration of salts in the system its electrical conductivity increases. Parallel with the increase in electrical conductivity the light absorption increases in the region of the spectrum in which

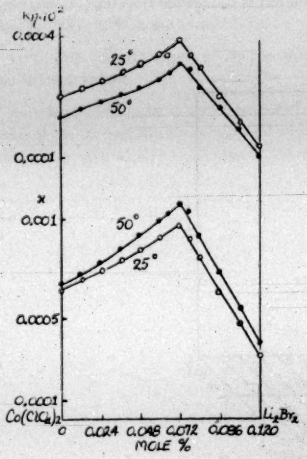

Fig. 5. Electrical conductivity and electrical conductivity, corrected for the viscosity, of the system $Co(ClO_4)_2-Li_2Br_2-(H_2O)-CH_3COC_2H_5$. Total salts 0.12 mole % (H_2O 0.72 mole %), $CH_3COC_2H_5$ 99.16 mole %.

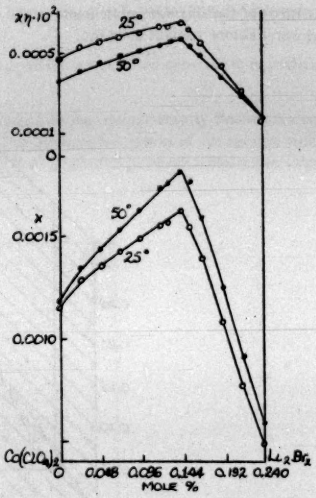

Fig. 6. Electrical conductivity and electrical conductivity, corrected for the viscosity, of the system $Co(ClO_4)_2-Li_2Br_2-(H_2O)-CH_3COC_2H_5$. Total salts 0.24 mole %, (H_2O 1.44 mole %), $CH_3COC_2H_5$ 98.32 mole %.

the cobaltous bromide complexes absorb. All of this points to the fact that the amount of cobaltous bromide complexes in the system increases with increase in the concentration of the salts.

The formation in the system of the compound $CoBr_2 \cdot 2LiBr$ is found only on the optical density-composition isotherms. The abscissa (composition) of the singular point on the optical density isotherms, corresponding to the compound $CoBr_2 \cdot 2LiBr$, remains constant with change in the equilibrium factors (temperature and concentration of salts). However, this singular point is not found on the κ-composition and $\kappa\eta$-composition curves due to the fact that the electrical conductivity does not possess the selectivity possessed by the light absorption. On the basis of this system it can also be seen that light absorption selectivity, differentiating it from the other properties of the system, makes a more complete study of the system possible.

System $CoBr_2 - Li_2Br_2 - (H_2O)$ – Methyl Ethyl Ketone

We studied two sections in the system $CoBr_2-Li_2Br_2-(H_2O)$–methyl ethyl ketone: total salts 0.12 mole % (H_2O 0.72 mole %), methyl ethyl ketone 99.16 mole %; and total salts 0.24 mole %, (H_2O 1.44 mole %), methyl ethyl ketone 98.32 mole %.

There are no literature data on the light absorption of cobaltous bromide solutions in methyl ethyl ketone.

The light absorption of cobaltous bromide solutions in methyl ethyl ketone increases in the 600-740 mμ region of the spectrum, reaching a maximum at 670 mμ.

The addition of lithium bromide to solutions of cobaltous bromide in methyl ethyl ketone shifts the absorption maximum toward the longer wave lengths.

The stronger absorption of divalent cobalt halide solutions in the 600-740 mμ region of the spectrum, as can be seen from the literature data and our studies, is associated with the appearance of cobaltous halide complexes in the solutions. The presence of light absorption in the portion of the spectrum corresponding to the lithium bromide-containing solutions of cobaltous bromide in methyl ethyl ketone indicates the presence of cobaltous bromide

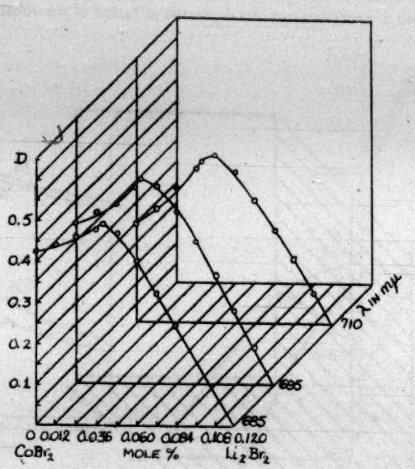

Fig. 7. Optical density of the system $CoBr_2-Li_2Br_2-(H_2O)-CH_3COC_2H_5$. Total salts 0.12 mole %, (H_2O 0.72 mole %), $CH_3COC_2H_5$ 99.16 mole %. Thickness of layer 1 mm.

complexes in the solutions. To determine their composition, the same as when studying the other systems, we analyzed the solutions by physicochemical methods, studying simultaneously with light absorption their electrical conductivity and viscosity.

In Fig. 7 are graphically represented the results of measuring the optical densities of the solutions in the given system with 0.12 mole % of total salts at 685, 695 and 710 mμ.

At 685 and 695 mμ each optical density-composition curve consists of two branches, intersecting at an angle in the maximum, the abscissa of which corresponds to the ratio between $CoBr_2$ and Li_2Br_2 of 2:1. The maximum corresponding to the given composition does not change its abscissa (composition) in the spectrum region 685-705 mμ. The formation in the system of the compound corresponding to this maximum can be expressed by the equation:

$$2CoBr_2 + Li_2Br_2 = 2(CoBr_2 \cdot LiBr).$$

In order to determine if the abscissa of the maximum, in which the branches of the optical density isotherms intersect, would change with change in the equilibrium factors we studied the section with 0.24 mole % of total salts. The measurement results for 695 and 710 mμ are shown in Fig. 8.

At 695 mμ the optical density-composition curve consists of two branches, intersecting in the maximum, the abscissa of which corresponds to a ratio between $CoBr_2$ and Li_2Br_2 of 2:1. Consequently, with a two-fold change in the concentration of the solutions, the abscissa of the maximum, corresponding fo the formation of the compound $CoBr_2 \cdot LiBr$ in the system, remains constant. With increase in the concentration of the solutions there is observed an increase in their optical density and a shifting of the optical density isotherm, on which the singular point stands out most clearly toward the longer wave lengths.

For the section with 0.12 mole % of total salts the singular point stands out most clearly on the optical density-composition curves at 685-690 mμ; on the optical density isotherms of the solutions with 0.24 mole % of total salts the singular point is most distinct at 695 mμ.

This shifting of the curves on the optical density-composition diagram, observed when the solution concentration is increased, is due to the decreased influence of the solvent on the light absorption properties of the cobaltous bromide complexes, and is associated with the decreased solvation of the cobaltous bromide complexes formed in solution.

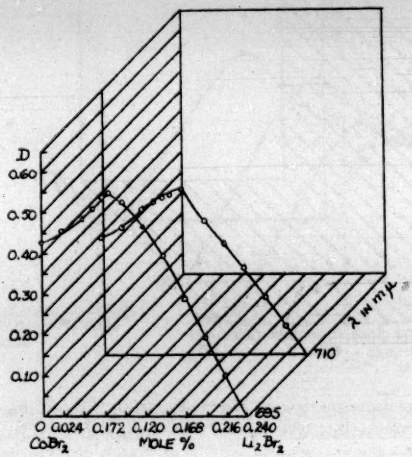

Fig. 8. Optical density of the system $CoBr_2-Li_2Br_2-(H_2O)-CH_3COC_2H_5$. Total salts 0.24 mole %, (H_2O 1.44 mole %), $CH_3COC_2H_5$ 98.32 mole %. Thickness of layer 0.5 mm.

To determine if the maximum point, observed on the optical density-composition curve, would be reflected on the isotherms of the other properties of the system, we studied the electrical conductivity and viscosity of the two sections of the system $CoBr_2-Li_2Br_2-(H_2O)$-methyl ethyl ketone with 0.12 and 0.24 mole % of total salts.

From Fig. 9, where the κ -composition and $\kappa\eta$ -composition curves for the section with 0.12 mole % of total salts are shown, it can be seen that the change in the electrical conductivity of the system as a function of its composition at 25 and 50° is depicted by a curve consisting of two branches, which mutually intersect in the maximum point, the abscissa of which corresponds to a ratio between $CoBr_2$ and Li_2Br_2 of 2:1.

The isotherm of the electrical conductivity at 50° is located over the isotherm of the electrical conductivity at 25°. When corrected for viscosity the order of the curves changes and there is a slight increase in the angle at which the branches of the $\kappa\eta$ -composition curve intersect. Each of the $\kappa\eta$ -composition curves consists of two branches, which intersect in the maximum point, the abscissa of which also corresponds to a ratio between $CoBr_2$ and Li_2Br_2 of 2:1.

A study of the electrical conductivity and viscosity of the solutions in the section with 0.24 mole % of total salts makes it possible to determine if the abscissa of the maximum on the electrical conductivity and $\kappa\eta$ isotherms will change with change in the concentration of the solutions. The κ -composition and $\kappa\eta$ -composition curves at 25 and 50° for the system with 0.24 mole % of total salts are shown in Fig. 10.

The general appearance of the electrical conductivity and $\kappa\eta$ -isotherms, shown in Fig. 10, is similar to that observed for the preceding section (Fig. 9).

The change in the electrical conductivity as a function of composition is expressed at 25 and 50° by a curve consisting of two branches, which intersect in the maximum point. The abscissa of this maximum corresponds to a

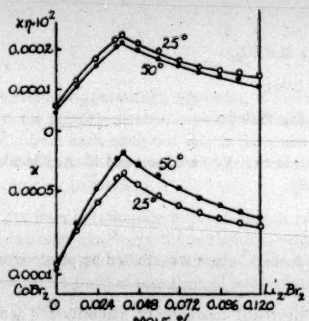

Fig. 9. Electrical conductivity and electrical conductivity, corrected for viscosity, of the system $CoBr_2$ – $-Li_2Br_2-(H_2O)-CH_3COC_2H_5$. Total salts 0.12 mole %, (H_2O 0.72 mole %), $CH_3COC_2H_5$ 99.16 mole %.

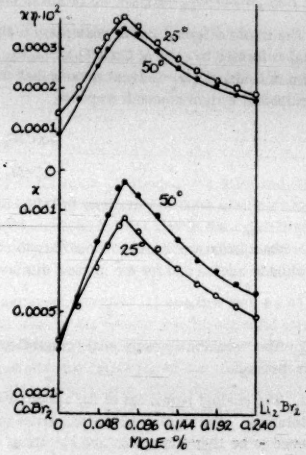

Fig. 10. Electrical conductivity and electrical conductivity, corrected for viscosity, of the system $CoBr_2$ – $-Li_2Br_2-(H_2O)-CH_3COC_2H_5$. Total salts 0.24 mole %, (H_2O 1.44 mole %), $CH_3COC_2H_5$ 98.32 mole %.

ratio between $CoBr_2$ and Li_2Br_2 of 2:1. The isotherm of the electrical conductivity at 50° is situated above the isotherm of the electrical conductivity at 25°, but the angle at which the branches of the electrical conductivity isotherms intersect is steeper for the section with 0.24 mole % of total salts than for the section with 0.12 mole % of total salts.

The $\kappa\eta$ -composition curves at 25 and 50° also consist of two branches, which mutually intersect in the maximum point, the abscissa of which corresponds to a ratio between $CoBr_2$ and Li_2Br_2 of 2:1. The angle at which the branches of each of the $\kappa\eta$ -composition curves intersect in this case also is steeper than for the corresponding curves of the section with 0.12 mole % of total salts. This is associated with the fact that with increase in the concentration of salts in the system the process for the formation of cobaltous bromide complexes in the system is augmented.

A study of the electrical conductivity and viscosity of the two sections of the system $CoBr_2-Li_2Br_2-(H_2O)$ – –methyl ethyl ketone at 25 and 50° revealed that the singular point found on the optical density isotherms corresponding to the formation of the compound $CoBr_2 \cdot LiBr$ in the system also shows up clearly on the κ -composition and $\kappa\eta$ -composition isotherms. The abscissa of this singular point remains constant with change in the equilibrium factors (concentration of salts and temperature).

An examination of the optical density-composition diagrams of the system $CoBr_2-Li_2Br_2-(H_2O)$–methyl ethyl ketone, shown in Figs. 7 and 8, reveals that with increase in wave length there is observed a maximum on the optical density-composition isotherms, also corresponding to the formation of a more complex cobaltous bromide compound in the system, which compound intensely absorbs light in the long wave length portion of the spectrum, but is considerably dissociated. The abscissa of this maximum on the optical density-composition curve at 710 mμ (Figs. 7 and 8) is found between the compositions corresponding to the compounds $CoBr_2 \cdot 2LiBr$ and $CoBr_2 \cdot LiBr$. As a result, on the optical density isotherms in the investigated system the formation of the compounds $CoBr_2 \cdot LiBr$ and $CoBr_2 \cdot 2LiBr$ is revealed; on the electrical conductivity and electrical conductivity corrected for viscosity, isotherms only the formation of compound $CoBr_2 \cdot LiBr$ is confirmed.

A study of the above presented systems, entering into the composition of the given quaternary reciprocal system, revealed that reaction between the salts is observed in the side system $CoBr_2-Li_2Br_2$–methyl ethyl ketone and in the diagonal system $Co(ClO_4)_2-Li_2Br_2$–methyl ethyl ketone. In the remaining side systems and in the diagonal system $CoBr_2-(LiClO_4)_2$–solvent we failed to observe any reaction between the salts.

The stable diagonal in the quaternary reciprocal system is formed by salts of $CoBr_2-(LiClO_4)_2$, the metastable diagonal is formed by salts of $Co(ClO_4)_2-Li_2Br_2$. A study of the system forming the metastable diagonal, and the side system $CoBr_2-Li_2Br_2$–solvent reveals that the formation of cobaltous bromide complexes in the given quaternary reciprocal system proceeds stepwise:

$$Co(ClO_4)_2 + Li_2Br_2 \rightleftharpoons CoBr_2 + 2LiClO_4,$$

$$2CoBr_2 + Li_2Br_2 \rightleftharpoons 2(CoBr_2 \cdot LiBr),$$

$$2(CoBr_2 \cdot LiBr) + Li_2Br_2 \rightleftharpoons 2(CoBr_2 \cdot 2LiBr).$$

In conclustion we consider it our duty to express our deep gratitude to I. V. Tananaev and M. A. Klochko for their valuable advice and for the interest displayed in the present study.

SUMMARY

1. The quaternary reciprocal system $Co(ClO_4)_2-Li_2Br_2$–methyl ethyl ketone was studied by physicochemical analysis methods.

2. The studied properties of the system were light absorption, electrical conductivity, viscosity and density of the solutions. The most sensitive properties relative to the formation of cobaltous bromide complexes in the system proved to be light absorption and electrical conductivity. The light absorption is not only a sensitive, but also a selective property.

3. The data, obtained in studying the light absorption of the system, were compared with the results of studying the other properties; here was taken into consideration the change in the equilibrium factors (concentration of salts and temperature) and the interaction of all of the components in the system.

4. Reaction between the salts was revealed in the diagonal system $Co(ClO_4)_2-Li_2Br_2$–methyl ethyl ketone and the side system $CoBr_2-Li_2Br_2$–methyl ethyl ketone.

5. Singular points are found on the optical density isotherms for each of these systems, indicating the formation of definite compounds in the system. The singular points on the optical density isotherms, corresponding to the formation of the compound $CoBr_2 \cdot LiBr$, are also found on the κ-composition and $\kappa\eta$-composition curves. The abscissas (compositions) of these points within the region of the stable phase remain constant with change in the equilibrium factors: temperature and concentration of salts.

6. The formation of the compound $CoBr_2 \cdot 2LiBr$ is also revealed on the optical density isotherms.

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COMPLEX FORMATION AND SOLID SOLUTIONS IN THE ADIAGONAL RECIPROCAL SYSTEM OF SODIUM AND POTASSIUM MOLYBDATES AND CHLORIDES

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Sodium and potassium, appearing as elements of the first group of the main subgroup of the third and fourth series in the periodic system, contrary to the usual representations on the great similarity of these elements, differ markedly from each other not only in the value of the ionic radii (0.98 and 1.33 A), but also in the crystalline structure of their salts and especially the character of the chemical reactivity of the salts, and, in particular, the character of complex formation.

The inter-relationship between sodium and potassium salts is extremely diverse: 1) in a few systems eutectics are formed with extremely limited solid solutions (NaF–KF [1]); 2) in most of the systems continuous solid solutions crystallize from the melts, which as a rule rarely reach low (room) temperatures, suffering decomposition in the majority of cases either into limited solid solutions (NaCl–KCl [2]) or with the formation of the compound Na_2SO_4–K_2SO_4 [3]); 3) much more rarely appear systems of sodium and potassium salts which directly deposit complexes from the melts at elevated temperature. To the latter belong the system of sodium and potassium molybdates, investigated by us.

Previous investigators of this binary system indicated the formation of a continuous series of solid solutions, which decompose only below the fusion curve with the formation of a single compound [4].

According to our data, sodium and potassium molybdates in melts form two compounds, the composition of which is apparently the following: $Na_2MoO_4 \cdot K_2MoO_4$ $Na_2MoO_4 \cdot 2K_2MoO_4$ (Fig. 1, Table 1).

To demonstrate the existence of these compounds we studied the reciprocal system of sodium and potassium molybdates and chlorides. The above-indicated compounds in the system Na, K ‖ Cl, MoO_4, the investigation results of which are given in the present paper, are represented by well-defined fields.

EXPERIMENTAL

The study was made by the visual-polythermal fusion method in a platinum crucible with platinum stirrer. A Pt–Pt, Pd, Au thermocouple was used. The original chlorides of C.p. quality were recrystallized. The molybdates were prepared by the fusion of the corresponding C.p. carbonates with freshly prepared MoO_3, taken in stoichiometric proportions. All of the compositions were expressed in equimolecular percents. Melting points of the salts: NaCl 800°, KCl 775°, Na_2MoO_4 688°, K_2MoO_4 926°.

Binary systems. Na_2MoO_4–K_2MoO_4. Studied by Amadori [4], then by I. N. Belyaev and M. L. Sholokhovich [5]. According to the data of these authors the fusion diagram is represented by a continuous series of solid solutions with a minimum. Our data differ in principle from the data of the previous authors. According to our data, on the fusion curve there exists a eutectic point at 667° and 19% K_2MoO_4 and two transition points at 686° and 37% K_2MoO_4 and 737° and 54% K_2MoO_4 (Fig. 1, Table 1).

Na_2Cl_2–Na_2MoO_4. Compounds melting without decomposition and with a flat maximum are formed, corresponding to the composition $Na_2Cl_2 \cdot 2Na_2MoO_4$, otherwise $NaCl \cdot Na_2MoO_4$ and 644°. Eutectic points: 628° and 58% Na_2MoO_4, 606° and 81% Na_2MoO_4 (Fig. 1, Table 1).

K_2Cl_2–K_2MoO_4. The eutectic point corresponds to 622° and 46% K_2Cl_2. In contrast to the preceding system, compound formation is absent (Fig. 1, Table 1).

Na_2Cl_2–K_2Cl_2. Studied by many authors [2, 6]. Represents a system with a continuous series of solid solutions with a minimum on the fusion curve at 660° and 50% Na_2Cl_2 (Fig. 1). The solid solutions decompose on cooling to about 500°, and within the reciprocal system around 610-620°.

TABLE 1

Binary Systems and Diagonal Sections

$Na_2MoO_4-K_2MoO_4$				$K_2MoO_4-K_2Cl_2$		$Na_2Cl_2-Na_2MoO_4$		$K_2MoO_4-Na_2Cl_2$		$Na_2MoO_4-K_2Cl_2$	
% K_2MoO_4	temperature	% K_2MoO_4	temperature	% K_2Cl_2	temperature	% Na_2MoO_4	temperature	% Na_2Cl_2	temperature	% K_2Cl_2	temperature
0	688°	40	697°	0	926°	0	800°	0	926°	0	688°
2	688	46	715	10	876	30	749	5	884	10	600
4	688	50	727	20	807	40	722	15	784	15	573
6	687	54	737	30	740	48	690	25	670	20	570
8	686	55	743	37.5	682	53	666	30	623	22.5	567
10	684	58	760	40	670	55	650	35	583	27.5	564
13	680	62	775	42.5	650	60	640	40	554	30	560
16	674	66	788	45	630	64	643	45	544	32.5	556
19	667	70	806	47.5	630	67	643	50	551	37.5	544
22	672	74	821	50	644	73	642	55	558	42.5	527
25	675	78	834	52.5	654	77	640	60	574	45	520
28	677	82	856	57.5	673	80	628	65	614	47.5	533
31	678	86	874	62.5	684	85	613	75	684	57.5	594
34	684	90	884	75	718	90	635	90	756	65	630
37	688	100	926	100	775	100	688	100	800	100	775

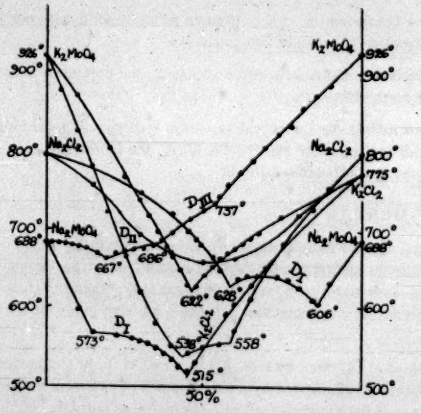

Fig. 1. Binary sides and diagonal sections of the system.

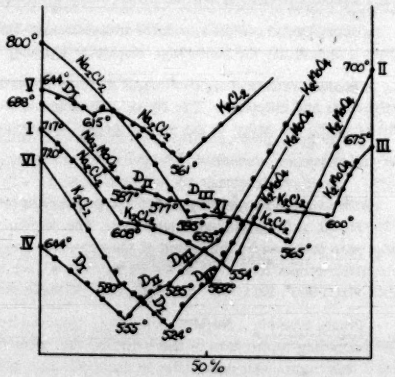

Fig. 2. Internal sections of the system I, II, III, IV, V, VI, XI.

Reciprocal system Na, K ‖ Cl, MoO_4. Seventeen internal sections were studied, of which two were diagonal sections (Figs. 1-4 and Tables 1-4).*

As can be seen from the projection of the fusion diagram of the system on the composition square, the surface of crystallization of the system consists of seven crystallization fields, four of which correspond to the components, while three of them correspond to the complexes of the two sides (Fig. 5).

* In order to avoid writing cumbersome formulas for the compounds shown in the diagrams and tables describing the sections, we will designate: $D_I = NaCl \cdot Na_2MoO_4$; $D_{II} = Na_2MoO_4 \cdot K_2MoO_4$; $D_{III} = Na_2MoO_4 \cdot 2K_2MoO_4$.

TABLE 2

Internal Sections.

Section III		Section VIII		Section IX		Section XI		Section XV	
60% K_2MoO_4 } → 40% K_2Cl_2 → Na_2Cl_2		90% Na_2MoO_4 } → 10% Na_2Cl_2 → K_2Cl_2		85% Na_2MoO_4 } → 15% K_2MoO_4 → K_2Cl_2		62% K_2Cl_2 } → 38% K_2MoO_4 → Na_2MoO_4		65% K_2Cl_2 } → 35% K_2MoO_4 → Na_2Cl_2	
% Na_2Cl_2	Temp.	% K_2Cl_2	Temp.	% K_2Cl_2	Temp.	% Na_2MoO_4	Temp.	% Na_2Cl_2	Temp.
0	675°	0	634°	0	675°	0	686°	0	692°
4	664	2.5	606	5	644	50	568	10	684
6	648	5	600	10	624	55	573	20	673
8	652	10	600	15	602	60	575	30	658
10	634	15	590	20	585	64	581	40	637
13	600	20	580	25	566	68	586	44	628
20	601	25	568	30	556	72	588	48	620
30	604	30	558	35	540	76	598	52	624
–	–	35	540	40	532	80	608	56	632
–	–	40	524	45	538	100	688	60	644
–	–	45	540	50	563	–	–	64	664
–	–	50	563	55	590	–	–	–	–
–	–	55	590	–	–	–	–	–	–
Intersection points at: 600° and 11% Na_2Cl_2		Intersection points at: 598 and 3.5% K_2Cl_2, 519° and 42% K_2Cl_2		Intersection points at: 644° and 5% K_2Cl_2, 580° and 23% K_2Cl_2, 521° and 43% K_2Cl_2		Intersection points at: 577° and 65% Na_2MoO_4, 587° and 74% Na_2MoO_4		Solid solutions	

TABLE 3

Internal Sections.

Section I		Section II		Section IV		Section XIII		Section XIV	
75% Na_2Cl_2 } → 25% K_2Cl_2 → K_2MoO_4		75% K_2MoO_4 } → 25% K_2Cl_2 → Na_2Cl_2		66% Na_2MoO_4 } → 33% Na_2Cl_2 → K_2MoO_4		65% K_2MoO_4 } → 35% K_2Cl_2 → Na_2MoO_4		85% K_2Cl_2 } → 15% K_2MoO_4 → Na_2Cl_2	
% K_2MoO_4	Temp.	% Na_2Cl_2	Temp.	% K_2MoO_4	Temp.	% Na_2MoO_4	Temp.	% Na_2Cl_2	Temp.
0	717°	0	770°	0	644°	0	706°	0	742°
5	700	10	680	10	612	35	662	10	732
10	680	15	636	20	578	40	653	15	722
20	632	20	602	25	560	45	648	20	711
25	608	25	565	28	556	50	645	25	720
30	606	30	580	31	578	60	637	30	686
35	600	40	594	37	592	65	635	34	676
40	590	45	596	40	596	68	634	38	670
45	585	50	596	43	610	71	635	42	663
50	576	55	595	47	618	77	640	46	656
55	562	60	626	50	633	80	642	50	650
60	574	65	656	54	653	83	651	54	648
65	614	70	688	57	668	86	659	58	650
		100	800	65	722	100	688	62	654
				75	783				
Intersection points at: 608° and 25% K_2MoO_4, 554° and 58% K_2MoO4		Intersection points at: 565° and 25% Na_2Cl_2, 595° and 54% Na_2Cl_2		Intersection points at 555° and 27% K_2MoO_4, 585° and 40% K_2MoO_4, 653° and 54% K_2MoO_4		Intersection points at: 644° and 47% Na_2MoO_4, 632° and 66% Na_2MoO_4, 640° and 79% Na_2MoO_4		Solid solutions	

TABLE 4

Internal Sections

Section V: 67% Na_2MoO_4 / 33% Na_2Cl_2 → K_2Cl_2		Section VI: 60% Na_2Cl_2 / 40% Na_2MoO_4 → K_2MoO_4		Section VII: 75% Na_2Cl_2 / 25% Na_2MoO_4 → K_2MoO_4		Section X: 80% K_2MoO_4 / 20% Na_2MoO_4 → K_2Cl_2		Section XII: 80% K_2MoO_4 / 20% K_2Cl_2 → Na_2MoO_4	
% K_2Cl_2	Temperature	% K_2MoO_4	Temperature	% K_2MoO_4	Temperature	% K_2Cl_2	Temperature	% Na_2MoO_4	Temperature
0	644°	0	720°	0	760°	0	850°	0	808°
10	628	10	666	30	590	5	828	12	783
13	623	15	637	33	566	10	800	20	771
16	615	20	607	35	554	15	780	28	750
19	622	23	590	37	554	20	752	32	736
22	618	26	594	39	534	25	722	36	724
25	610	29	564	43	524	30	698	40	710
31	596	35	540	47	515	32.5	682	44	694
37	578	38	530	48	533	35	667	48	684
40	568	41	524	50	545	37.5	652	52	697
43	561	44	552	52	556	40	640	56	696
45	570	50	574	54	566	42.5	626	60	693
50	586	53	595	56	579	45	612	64	665
55	603	56	614	58	591	47.5	622	68	667
60	623	59	626	–	–	50	630	72	669
		64	692						
Intersection points at: 615° and 16% K_2Cl_2, 561° and 43% K_2Cl_2.		Intersection points at: 580° and 23% K_2MoO_4, 524° and 40% K_2MoO_4, 582° and 52.5% K_2MoO_4.		Intersection points at: 549° and 35% K_2MoO_4, 515° and 46% K_2MoO_4.		Intersection point at: 602° and 46% K_2Cl_2.		Intersection points at: 684° and 46% Na_2MoO_4, 662° and 66% Na_2MoO_4.	

In Fig. 6 is shown the projection of the mutual crystallization curves on the plane of the polytherm of the binary system Na_2MoO_4–K_2MoO_4, with the aid of which the ternary nonvariant points were made precise. The isotherms, drawn through 50°, make it possible to depict the space model of the reciprocal system Na, K ‖ Cl, MoO_4.

The division into phase triangles basically proceeds from the apex of the compound $NaCl \cdot Na_2MoO_4$ (Fig. 4), melting without decomposition, which appears as the pole of a three-pointed star. Not one of the triangulation sections fails to have the character of binary systems, as a result of which we have four ternary transition points and only one eutectic point E_{II} 507°, which corresponds to the most characteristic internally inscribed triangle $NaCl \cdot Na_2MoO_4$–$Na_2MoO_4 \cdot 2K_2MoO_4$–$K_2Cl_2$. The nonvariant ternary eutectic and transition points possess the index of the corresponding phase triangle. Eutectic inversion points are absent in the system.

In Table 5 in the last column are presented the equilibrium phases, forming the apexes of the phase triangles (Fig. 4).

TABLE 5

Temperatures and Compositions of the Nonvariant Points

Nature of point	Temperature	Composition (in %)				Equilibrium phases
		Na_2Cl_2	K_2MoO_4	Na_2MoO_4	K_2Cl_2	
Transition P_I	527°	41	53.5	5.5	–	K_2Cl_2, K_2MoO_4, $Na_2MoO_4 \cdot 2K_2MoO_4$
Eutectic E_{II}	507	42	47	11	–	K_2Cl_2, $NaCl \cdot Na_2MoO_4$, $Na_2MoO_4 \cdot 2K_2MoO_4$
Transition P_{III}	543	30	35	35	–	$NaCl \cdot Na_2MoO_4$, $Na_2MoO_4 \cdot 2K_2MoO_4$, $Na_2MoO_4 \cdot K_2MoO_4$
Transition P_{IV}	560	19	24	57	–	$NaCl \cdot Na_2MoO_4$, $Na_2MoO_4 \cdot K_2MoO_4$, Na_2MoO_4
Transition P_V	524	49.5	41.5	9	–	Na_2Cl_2, K_2Cl_2, $NaCl \cdot Na_2MoO_4$

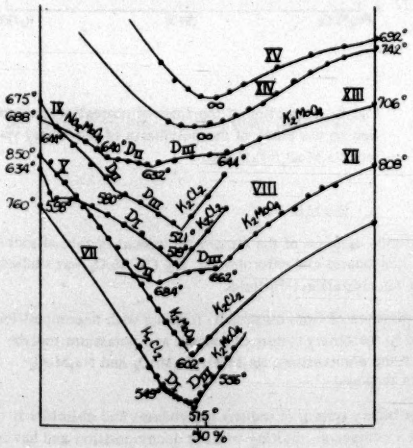

Fig. 3. Internal sections of the system VII, VIII, IX, X, XII, XIII, XIV, XV.

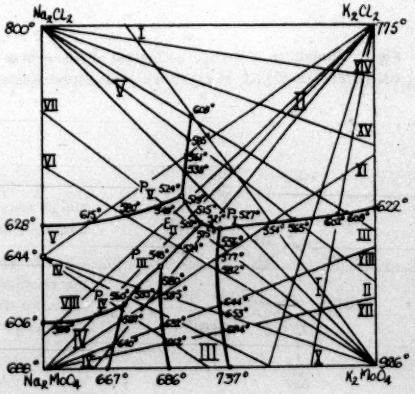

Fig. 4. Location of the internal sections and triangulation of the system Na, K ‖ Cl, MoO_4.

The fundamental equations which characterize the reactions between the components in the system are as follows:

$$3Na_2Cl_2 + 2K_2MoO_4 = Na_2Cl_2 \cdot 2Na_2MoO_4 + 2K_2Cl_2,$$

$$Na_2Cl_2 + 3K_2MoO_4 = Na_2MoO_4 \cdot 2K_2MoO_4 + 2K_2Cl_2,$$

$$7Na_2MoO_4 + 2K_2Cl_2 = 2(Na_2Cl_2 \cdot 2Na_2MoO_4) + Na_2MoO_4 \cdot 2K_2MoO_4,$$

$$4Na_2MoO_4 + K_2Cl_2 = Na_2Cl_2 \cdot 2Na_2MoO_4 + Na_2MoO_4 \cdot K_2MoO_4.$$

The topology of the system Na, K ‖ Cl, MoO_4 is exceedingly odd. The topological scheme of the crystallization tree is shown in Fig. 7. The eutectic tree has a branched line appearance with a concealed ternary eutectic point, not connected with the nonvariant points of the side binary system.

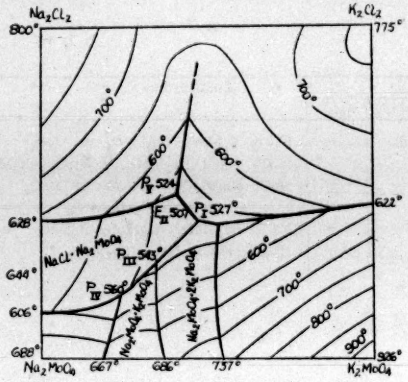

Fig. 5. Projection of the space diagram of the reciprocal system Na, K ‖ Cl, MoO_4 on the composition square.

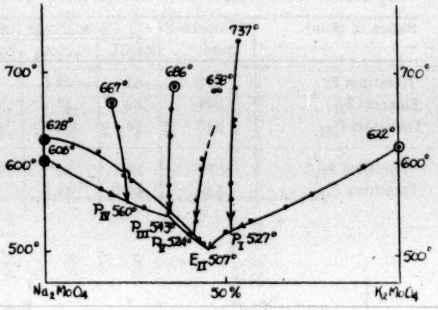

Fig. 6. Projection of the lines of mutual crystallization on the plane of the polytherm of the binary system Na_2MoO_4–K_2MoO_4.

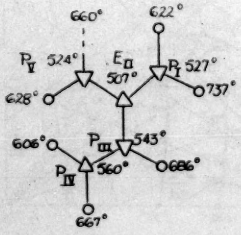

Fig. 7. Scheme of the eutectic phase complex in the system.

SUMMARY

1. The fusion diagram of the ternary reciprocal system of sodium and potassium molybdates and chlorides Na, K ‖ Cl, MoO_4 was studied, consisting of seven crystallization fields.

2. The presence of two compounds, melting with decomposition, was established in the binary system of sodium and potassium molybdates, for which the compositions $Na_2MoO_4 \cdot K_2MoO_4$ and $Na_2MoO_4 \cdot 2K_2MoO_4$ were proposed.

3. In the binary system of sodium molybdates and chlorides it was shown that a compound, melting without decomposition and having the composition $NaCl \cdot Na_2MoO_4$ exists at 644°; a similar type of compound is absent in the corresponding potassium system.

4. The system Na, K ‖ Cl, MoO_4 belongs to the adiagonally-reversible type of reciprocal systems and is characterized by the presence of an internally inscribed phase triangle, resting on the poles of two complexes and the potassium chloride apex opposite to them.

5. The tree of the eutectic phase has a branched line appearance and a concealed ternary eutectic point, not coming in contact with the nonvariant points of the binary sides.

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* See Consultants Bureau Translation, page 1331.

STUDY OF VANADIUM REDUCTION AT THE DROPPING MERCURY CATHODE ON A POTASSIUM CHLORIDE SUPPORT

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The literature data dealing with the reduction of vanadium on a potassium chloride support are few and contradictory. Zeltzer [1] observed a well-defined wave with $E_{1/2} = -0.85$ V (s.c.e.)* when he reduced vanadium trichloride in an inert electrolyte, consisting of 0.1 N potassium chloride and 0.01 N hydrochloric acid. However, Kolthoff and Lingane [2] believe that the vanadium trichloride solutions used by Zeltzer were partially oxidized to vanadic salts, and that for this reason it is difficult to decide to which type of vanadium reduction this wave corresponds. Lingane [3], in studying the reduction of trivalent vanadium on a potassium chloride support, observed a number of entangled waves, for which he considered the determination of the half-wave potentials to be meaningless.

To determine if it is possible to reduce vanadium ions on a potassium chloride support is of definite interest for a number of reasons: the potassium chloride creates a nearly neutral medium in the solution, the chloride ions fail to form complexes with the vanadium ions, etc.; consequently, the purpose of the present work was to make a polarographic study of the reduction of vanadium in different valence states with the use of a potassium chloride solution as the inert electrolyte.

EXPERIMENTAL

All of the measurements were made on a visual polarograph built by the UBAS.** The characteristics of the mercury-dropping electrode were: $m^{2/3}t^{1/6} = 2.33$ mg$^{2/3}$sec$^{-1/2}$, $t = 3.20$ sec. The height of the column of mercury was maintained constant in all of the experiments. A normal calomel half-element served as the anode: the constancy and accuracy of the latter potential was checked by the half-wave potential of thallium, taken as the standard ($E_{1/2}$ of thallium in 1.0 N potassium chloride solution is equal to -0.48 V). The force of the diffusion current was measured with the aid of a mirror galvanometer having a sensitivity of $7.6 \cdot 10^{-9}$ A/cm/m, provided with a transparent scale 500 mm in length.

Before each experiment purified nitrogen was passed through the investigated solution (its volume was about 20-25 ml) for 20 minutes to remove dissolved oxygen. The experiments were run in a thermostat at 25° ± 0.5.

The half-wave potentials were determined graphically.

A solution of vanadium oxychloride, $VOCl_2$, was prepared by the reduction of freshly precipitated vanadium pentoxide with concentrated hydrochloric acid. The concentration of the obtained solution was determined by titration with a standard solution of a ferrous salt, using phenylanthranilic acid as the indicator [4]. Solutions of the di- and trivalent vanadium salts were obtained by the respective reduction of pentavalent vanadium with sodium amalgam and bismuth [6].

From polarograms obtained on a support of 1.0 N potassium chloride, shown in Fig. 1, it can be seen that the vanadyl ion gives a very distinct wave with a half-wave potential of -1.0 V, (Curve 2). On the polarogram, obtained under the same conditions in a solution of pentavalent vanadium (Curve 1), there exist two well-defined waves with half-wave potentials of -0.32 and -1.0 V, respectively. The fact that the half-wave potential for the second reduction stage of pentavalent vanadium coincides with the value of the half-wave potential for the reduction of the vanadyl ion can be explained as being due to the fact that while the wave with $E_{1/2} = -0.32$ V corresponds to the reduction of pentavalent vanadium to the tetravalent state, the wave with $E_{1/2} = -1.0$ V in both cases corresponds to the further reduction of the vanadyl ion to V^{II}.

The solution of trivalent vanadium, partially oxidized to the tetravalent state (Curve 3), under the same conditions gives two well-defined waves: the first with $E_{1/2} = -0.52$ V and the second with $E_{1/2} = -1.0$ V. It can be seen that the second of these waves fully supports the just-expressed postulation.

* s.c.e. — saturated calomel electrode. All of the half-wave potential values given below are relative to s.c.e.

** Ural Branch of the Academy of Sciences.

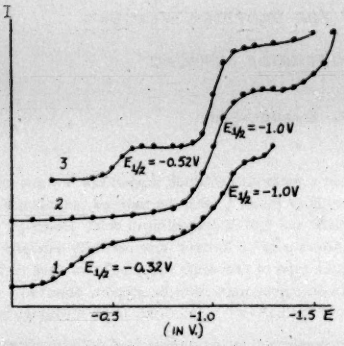

Fig. 1. Polarograms, obtained on a support of 1 N potassium chloride for solutions containing: pentavalent vanadium ions (1), vanadyl ions (2), trivalent vanadium ions (3).

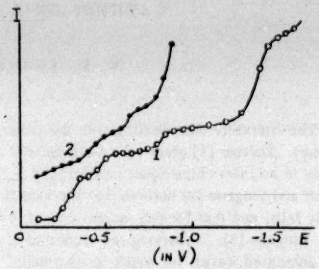

Fig. 2. Polarograms, obtained on a support of 0.1 N potassium chloride for solutions containing: pentavalent vanadium ions (1), trivalent vanadium ions (2).

At potassium chloride concentrations lower than 1.0 N the tri- and pentavalent vanadium ions give confusing polarograms, containing several very ill-defined waves (Fig. 2).

A solution of a divalent vanadium salt on a support of 1.0 N potassium chloride failed to give a cathode wave. The studies of other authors also failed to give any data suggesting the reduction of vanadium to the metal. From this it is to be concluded that the reduction of vanadium (III) in 1.0 N potassium chloride proceeds only to vanadium (II) and that $E_{1/2}$ of the corresponding wave is equal to −0.52 V.

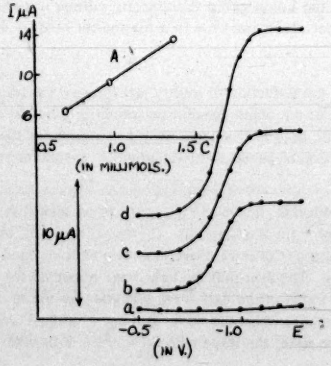

Fig. 3. Polarographic waves formed by the vanadyl ion in 1.0 N potassium chloride at vanadyl concentrations of: 0 (a), 1.464 millimol/liter (b), 2.196 millimol/liter (c), 2.928 millimol/liter (d). A) Force of the diffusion current as a function of vanadyl ion concentration.

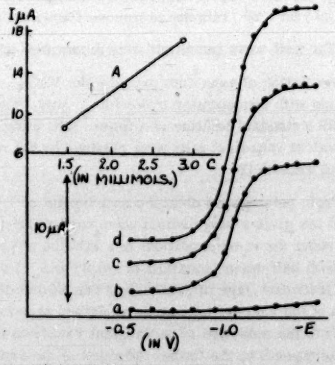

Fig. 4. Polarographic waves formed by the vanadyl ion on a support of 0.1 N potassium chloride at vanadyl concentrations of: 0 (a), 0.677 millimol/liter (b), 0.948 millimol/liter (c), 1.354 millimol/liter (d). A) Force of the diffusion current as a function of vanadyl ion concentration.

A wave corresponding to the anodic oxidation of divalent vanadium was observed by us; this agrees with the data of Lingane that divalent vanadium is oxidized at the dropping mercury electrode in both dilute acid solutions [3] and in one molar solutions of either potassium fluoride or bromide [5].

Further it was established by us that with decrease in the concentration of the inert electrolyte – potassium chloride – the half-wave potential for the reduction of the vanadyl ion is shifted toward more positive values, which is shown in the table.

Concentration of potassium chloride (in moles/liter)	$E_{1/2}$ (in V)
1.0	−1.0
0.1	−0.92
0.05	−0.88

To determine if the amount of vanadium existing as the vanadyl ion could be quantitatively determined by the polarographic method, a study was made of the relationship between the force of the diffusion current and the vanadyl salt concentration on a support of 1.0 and 0.1 N potassium chloride solutions.

As can be seen from Figs. 3 and 4, the presence of direct proportionality between the indicated values was established.

SUMMARY

1. The reduction of vanadium at the dropping mercury cathode on a support of 0.1-1.0 N potassium chloride solutions, taken as the inert electrolyte, was studied.

2. It was shown that there are two waves on the polarogram of the pentavalent vanadium solution, the first of which with $E_{1/2} = -0.32$ V corresponds to the reduction of pentavalent vanadium to the tetravalent state, and the second with $E_{1/2} = -1.0$ V to the reduction of tetravalent vanadium to the divalent state. The polarogram of the vanadyl salt solution has only one wave with $E_{1/2} = -0.52$ V, which corresponds to the reduction of trivalent vanadium to the divalent state. Further reduction of vanadium to the metal was not established.

3. A direct relationship was found to exist between the force of the diffusion current and the vanadium ion concentration, which creates precedents for the development of a method for the polarographic determination of vanadium as the vanadyl ion on a support of potassium chloride.

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THE DEVELOPMENT OF BINARY ALLOY PHASE DIAGRAMS IN CONNECTION WITH PARTICLE REACTIVITY BETWEEN FUSIBLE ELEMENTS

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The existing phase diagrams of binary alloys in the majority of cases are taken by us as being separate types of phase diagrams, whereas in reality there should exist a well-defined bond and inter-relationship between them. This follows from the fact that, characterizing reactivity between fusible elements, the phase diagrams should undoubtedly show not only all of the gradations of possible element combinations, but also the transition of these gradations from one form into another. Actually, on this score A. A. Bochvar indicates that "some rules on the construction of phase diagrams of one component with a whole series of other components have already been assembled", but, "unfortunately the number of such rules is still extremely few [1]."

It is also necessary to mention that Soviet investigators [2-4], making use of the representation of intermolecular reaction between components, made a whole series of interesting calculations, associated with the theoretical construction of a number of phase diagrams for alloys. However, these calculations do not pursue the goal that we have set ourselves. As was already stated, the important consideration for the theory of alloys is the generalization of existing phase diagrams, the establishing between them of internal bonds as the result of reactivity development between them or other fusible elements.

Realizing that all developments proceed from simple to complex, it is necessary to take as the starting phase diagram one that is depicted by weak, or in the limiting case complete absence, chemical reactivity between the fusible elements.*

In studying different binary diagrams, is it possible to follow, even if only in general form, the original nature of the corresponding reactions between elements in alloys? Realizing that the external form (outline) of the diagram is undoubtedly characterized by containing internal processes, operating under definite conditions in the given systems, it is possible, on the basis of this, to unconditionally give a positive answer to the just posed question.

From practice it is known that reactivity between elements is usually accomplished by supplying different amounts of heat to the system (if the given elements are at all inclined to react).

Among available systems it is easy to find those in which the fusible elements begin to react, when found in the liquid state, i.e., at elevated temperatures.**

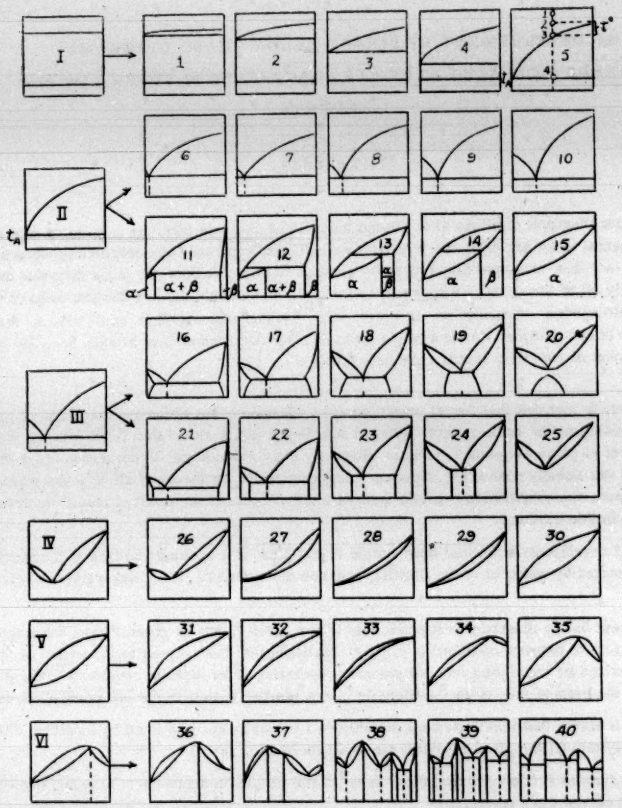
In the table, the top row of phase diagrams (from 1 to 5) in its schematic outline represents the increase in reactivity between different elements, beginning from their complete (or almost complete) inertness and going to their complete and mutual solubility in the liquid form.

Diagram 5 shows that on cooling the system to Point 2 the energy of reaction A $\longleftarrow\longrightarrow$ B does not permit the B particles to separate in the pure form; consequently, a certain degree of supercooling in t° is required so as to enable the process for the crystallization of pure B to begin. In other words, at Point 3 the homonymous bonds B $\longleftarrow\longrightarrow$ B begin to relatively prevail over the heteronymous bonds A $\longleftarrow\longrightarrow$ B. Below Point 4 the homonymous bonds B $\longleftarrow\longrightarrow$ B and A $\longleftarrow\longrightarrow$ A obtain an absolute advantage over the bonds A $\longleftarrow\longrightarrow$ B, consequently the system completely decomposes into its component parts A and B.

However, is it possible to calculate in such a way that the existence of intermediate links between systems 1 and 5 is avoided? In nature with her inexhaustible possibilities there should unconditionally also be found such

* Following the teachings of D. I. Mendeleev, we associate the phase solubility of one element in another with the appearance in the given system of chemical reactivity between heterogeneous particles.

** It is known that certain elements can react when found in the solid state, forming solid solutions and chemical compounds. But these cases, characterizing the more complex interrelationships between fusible elements, should find their place in the later stages of phase diagram development.



Phase Diagrams of Binary Alloys.

reaction pairs in which the energy of the heteronymous bonds in the liquid state can possess only extremely limited significance, vanishing with relatively slight degrees of supercooling in the system (Diagrams 1, 2, 3, 4).

However, when Diagram 5 is regarded as being a certain stage in the path of reactivity development between fusible elements it is evident that another case that can present itself is where the energy of the heteronymous bonds A ← → B can be overcome only when the system is supercooled below the crystallization temperature of the low melting element t_A. Actually, such systems exist, forming alloys with so-called eutectics.

The second row of phase diagrams in the table represents the development of reactivity between elements that form eutectics. Here the energy of reaction of the elements in the liquid state grows from one diagram to the next, in which connection the "depth" of the eutectic point in essence refers to the magnitude of the heteronymous bonds A ← → B, existing in the liquid alloy.*

* As regards the greater or lesser shifting of the eutectic point toward the low melting element, this is explained by the different magnitude of the homonymous bonds A ← → A and B ⇇ ⇉ B. The more the homonymous bond B ⇇ ⇉ B prevails over the homonymous bond A ← → A, the greater should be the displacement of the eutectic point in the direction of the low melting element A [5].

The diversity of natural combinations of elements with each other attracts the appearance in alloys of not only liquid, but also solid solutions.

Certain combinations of the mentioned solutions give diagrams with peritectics, which in a somewhat modified form are also developed from the original Diagram II (third row of phase diagrams in the table).

The final conclusion of peritectic diagrams is the diagram that is characterized by complete solubility of the elements, both in the liquid and in the solid state (Diagram 15).

If the phase diagrams with peritectics are depicted in the final end as mechanical mixtures of solid solutions α and β (or solid solution with one of the pure elements), but in this connection not all of the alloys form eutectics in the complete sense of the word, then the case where the formation of eutectics and solid solutions is realized in one and the same alloy becomes possible.

Appropriate modifications of the phase diagrams are shown in the fourth and fifth rows of the table. Although both of these rows of phase diagrams end in approximately the same type of diagram (Diagrams 20 and 25), nevertheless the diagrams of the fourth row to some degree still characterize the tendency for the appearance of homonymous bonds in alloys, to the extent that solid solutions tend to change their concentration.

Such a tendency is not present in the diagrams of the fifth row, consequently, the concluding Diagram 25 can be taken as characterizing the system in which a completely stable solid solution is formed.

From this diagram can be developed the diagrams for complete solid solutions of the type of Diagram 15, not by way of changing the solidus line, as was done in the case of developing the phase diagrams with peritectics (Diagrams 11-14), but instead by way of modifying the liquidus line, which actually denotes a decrease from one alloy to the next in the values of the heteronymous bonds in the liquid state (Diagrams 26-30).

If phase diagram 30 is taken as the original and a search is made for the systems in which a systematic increase in the magnitude of the heteronymous bonds in the solid state is possible, then it becomes possible to obtain the seventh row of diagrams, in which the concluding phase diagram (35) characterizes the system with a definite chemical compound (daltonide type).

The last row of phase diagrams serves to illustrate the development of systems with two chemical compounds.

In principle it is possible to give the development of phase diagrams with any number of chemical compounds, to the extent that all of the fundamental element combinations received their characterization in the presented series.

SUMMARY

1. The existing types and forms of phase diagrams of binary alloys can be systematized by that degree of reactivity that is characterized by these diagrams.

2. The development of the phase diagrams proceeds from complete inertness of the given elements to their complete reaction in the liquid and then in the solid states. Passing through different gradations and modifications, reactivity of such nature between the elements can be achieved if in the given system the appearance of one or more definite chemical compounds is possible.

This, in essence, is the limiting expression of heteronymous bonds, which is confirmed by the fact that any diagram with chemical compounds represents a combination of simple diagrams.

3. It is possible that the scheme given in the table for the arrangement of the phase diagrams of binary alloys will require some sort of modification and improvement. Nevertheless, in our opinion, any modification of the scheme should remain within the limits of the following basic principles: 1) the development of phase diagrams should proceed from simple to complex, 2) the development of phase diagrams in itself actually presupposed the development of reactivity between elements (from partial and weak to more complete and profound reactions).

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MOLECULAR REFRACTION OF CARBOXYLIC ACID AMIDES

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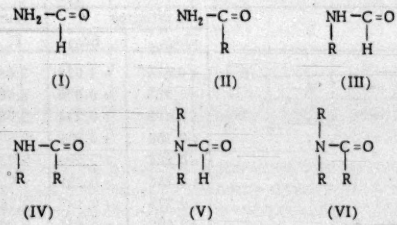
As is known, the molecular refraction of nitrogen compounds strongly depends on their structure; here one of the least studied remains the question of structural influences on the refraction of acid amides.

Eisenlohr [1, 2] regarded amide groups as "hidden conjugation" systems. From the viewpoint of Eisenlohr, the molecular refractions of amides, the same as for conjugated compounds, should be characterized by specific exaltation values, which are reduced due to "conjugation disturbance" by alkyl radicals R in the transition from formamide (I) to its homologs (II) and from primary amides to secondary and tertiary amides.



(I) (II) (III)

(IV) (V) (VI)

On the basis of what has been said the amides were excluded by Eisenlohr from the number of compounds for which the refractions can be calculated directly from the tables set up for them [2, 3].

Auwers [4], adding his own measurements to the literature data, came to the conclusion that considerable variations in the experimental data do not permit making any definite conclusions as to the influence of structure on the refraction of amides. Together with this, Auwers proposed supplementing the tables of Eisenlohr with the atomic refraction value for amide nitrogen, common to all types of amides and equal (for line D) to 2.606. The considerable deviations from this average value Auwers deemed possible to neglect, thus leaving unanswered the question of the effect of structural influences on the atomic refraction of the nitrogen in amides.

In general, the new atomic and group refraction tables of Vogel [5] fail to have any special data for amide groups since this class of compounds was not investigated by Vogel and coworkers.

The question as to the possibility and accuracy of calculating the molecular refractions of amides from the system of refraction bonds [6] also remains unanswered.

To determine the relationship existing between the refraction of amides and their structure, and with the purpose of supplementing the existing tables of refraction constants, we prepared 12 amides of the simpler carboxylic acids in pure form. We considered it possible to limit the study to secondary and tertiary amides, since the primary amines (other than formamide) are crystalline, and refractometry is usually not used for their study.

In treating the experimental data we came to use only our own materials, since it was revealed that the published physicochemical constants for secondary and tertiary amides are unreliable. Previous investigators failed to devote the necessary attention to purification of the obtained compounds, in addition to which the acylation products of the amines or the dehydration products of their salts always contain volatile salts as impurities, which it is impossible to remove by distillation only. The salt impurities have very little effect on the refractive index, but they markedly increase the density and lower the molecular refraction values.

In Table 1 the density values for the amides, described earlier by Auwers [4] and Bruhl [7], are compared with the data for our preparations, subjected to special purification, as is indicated in the Experimental part. It is not difficult to see that the preparations of Auwers and one of Bruhl's preparations have considerably higher densities and probably are insufficiently pure. A difference in the densities of the order shown in Table 1 can easily lead to a lowering of the molecular refraction by 0.5% and more, masking in this way the effect of structural influences.

TABLE 1

Density Comparisons of the Synthesized Amides with the Literature Data

Amide	d_4^{20}		Difference
	our preparation	literature data	
Dimethylformamide	0.9486	0.9508 [7]	−0.0022
Dimethylacetamide	0.9437	0.9434 [7]	+0.0003
Ethylacetamide	0.9237	0.9279* [4]	−0.0042
Diethylacetamide	0.9045	0.9110** [4]	−0.0065

Our data, presented in Table 2, testify to the fact that the molecular refraction exaltations EM_D and $E\Sigma_D$, calculated according to Eisenlohr, show a definite relationship to the structures of amides. The mean exaltation values EM_D for different types of amides prove to be the following: (I) + 0.485, (III) + 0.25 ± 0.07, (IV) + 0.26 ± 0.01, (V) −0.11 ± 0.02, (VI) −0.33 ± 0.04.

TABLE 2

Atomic Refractions of Nitrogen in Amides and the Molecular Refraction Exaltation for Amides, Calculated According to the Scheme of Eisenlohr [1, 2, 3]

Type of structure	Amide	Exaltation		Atomic refractions of nitrogen		
		EM_D	$E\Sigma_D$	C	D	F
I	Formamide	+0.485	+1.078	2.689	2.707	2.774
III	Methylformamide	+0.223	+0.378	2.708	2.725	2.804
III	Ethylformamide	+0.173	+0.234	2.655	2.673	2.755
III	n-Butylformamide	+0.356	+0.352	2.827	2.858	2.933
IV	Ethylacetamide	+0.256	+0.294	2.739	2.758	2.843
IV	n-Butylacetamide	+0.256	+0.223	2.733	2.758	2.837
IV	n-Butylbutyramide	+0.279	+0.197	2.762	2.781	2.863
V	Dimethylformamide	−0.093	−0.127	2.724	2.747	2.840
V	Diethylformamide	−0.136	−0.135	2.681	2.704	2.798
VI	Dimethylacetamide	−0.381	−0.438	2.440	2.459	2.546
VI	Diethylacetamide	−0.346	−0.301	2.480	2.494	2.587
VI	Dimethylbutyramide	−0.341	−0.296	2.475	2.499	2.581
VI	Di-n-butylbutyramide	−0.260	−0.131	2.567	2.580	2.676

On going from formamide (I) to tertiary amides (VI) the exaltation in general decreases, being depressed in accord with the viewpoint of Eisenlohr. However, the exaltations for types (III) and (IV) prove to be practically the same, although for secondary amides with a twice disturbed "conjugation" (IV), according to Eisenlohr, values lower by 0.2 than for type (III) should be expected.

The specific exaltations $E\Sigma_D$ follow the same rule, but by no means show a greater constancy than EM_D when the molecular weight is changed. For amides of type (IV) and (VI) a tendency is noted for reduction of the absolute values of $E\Sigma_D$ with increase in the molecular weight.

However, from the purely practical viewpoint, the calculation of amide molecular refractions by the scheme of Eisenlohr, using three different atomic refraction values for the nitrogen and six normal exaltation values for the different types of amides (I-VI), is clearly irrational. A study of the data obtained by us reveals that the molecular refractions of all liquid amides can be accurately calculated using a total of only two atomic refraction constants for the amide nitrogen. As can be seen from Table 2, the atomic refraction of nitrogen in the amides of type (I), (III), (IV) and (V) fluctuates within the narrow limits of 2.67 to 2.86 around the mean value of 2.750 ± 0.038 (for line D). In the tertiary amides of type (VI) the atomic refraction of the nitrogen is lower by approximately 0.2: from 2.46 to 2.58, and on the average is 2.508 ± 0.036 (line D). It is interesting to mention that the tertiary amides of this type also occupy a singular position among carboxylic acid amides as regards chemical properties. Thus, for example, they are hydrolyzed much more slowly in acid medium and saponified with much greater difficulty by alkalis than the primary and secondary amides or the tertiary formamides. Consequently, the refraction tables of Eisenlohr [2, 3] should be supplemented with two new atomic refraction constants for the nitrogen found in the different types of amides. To ignore the difference between the indicated two groups of amides and recommend the

* Calculated from $d_4^{15.8}$ with the aid of the temperature coefficient $\frac{\Delta d}{\Delta t} = -0.00076$ found by us.

** Calculated from $d_4^{17.4}$ with the aid of the density temperature coefficient −0.00078.

TABLE 3

Refractions of Amide Groups and Refractions of C−N Bonds in Amido Groups (From the Tables of Vogel [5, 6])

Type of structure	Amide	Refractions of the −CON< group in amides of type (VI) or of the −CONH− group in the remaining types of amides			Refractions of the C−N bond in the amido groups −CON<			Differences between the experimental and calculated, from the bond refractions of Vogel [6], values of MR_D
		C	D	F	C	D	F	
I	Formamide	8.518	8.582	8.720	2.081	2.122	2.173	+ 0.552
III	Methylformamide . .	8.528	8.596	8.746	1.904	1.923	1.996	+ 0.353
III	Ethylformamide . . .	8.449	8.518	8.672	1.825	1.844	1.930	+ 0.274
III	n-Butylformamide. .	8.586	8.661	8.807	1.954	1.976	2.077	+ 0.406
IV	Ethylacetamide . . .	8.527	8.599	8.755	1.889	1.902	2.002	+ 0.332
IV	n-Butylacetamide. .	8.483	8.556	8.706	1.837	1.848	1.965	+ 0.278
IV	n-Butylbutyramide .	8.456	8.511	8.688	1.821	1.819	1.959	+ 0.249
V	Dimethylformamide	8.535	8.614	8.797	1.724	1.728	1.824	+ 0.158
V	Diethylformamide. .	8.446	8.519	8.687	1.635	1.631	1.753	+ 0.061
VI	Dimethylacetamide.	7.216	7.294	7.464	1.417	1.413	1.513	−0.157
VI	Diethylacetamide. .	7.210	7.278	7.434	1.411	1.395	1.523	−0.175
VI	Dimethylbutyramide	7.194	7.264	7.425	1.406	1.399	1.516	−0.171
VI	Di-n-butylbutyramide	7.166	7.209	7.366	1.362	1.320	1.517	−0.250

use of one general refraction increment for the amide nitrogen, as was done by Auwers [4], would be incorrect. The divergence between the proposed mean values for the atomic refraction of the amide nitrogen is considerably greater than the difference between the atomic refractions of hydroxyl and ether oxygen, and is of the same order as the difference between the constants for nitrogen in primary, secondary and tertiary amines, oximes and alkylideneamines. In addition to this, different atomic refraction values are used in the enumerated cases.

The refraction table of Vogel [5], calculated on the basis of newer and more homogeneous experimental material, and chiefly containing group refractions, should be supplemented by the group refractions for the group −CON< in the tertiary amides $RCONR'_2$ and the group HCON< or −CONH− in formamides and the secondary amides of other carboxylic acids. The mean values of these group refractions for three spectral lines, calculated from the data in Table 3 and presented in Table 4, permit calculating the molecular refraction of amides with an accuracy of ± 0.04.*

In recent years, the tables of bond refractions (instead of atomic refractions) are steadily finding greater use. One of the arguments in favor of the preferred use of bond refractions is the indication that it is possible to do with a fewer number of refractometric constants in a number of cases.

It was of interest to check the possibility of applying the bond refractions of Vogel [6] to the amides of carboxylic acids. The calculation results, given in Table 3, show that the refraction values for C−N and N−H, established by Vogel and coworkers on aliphatic amines, are unsuitable for the accurate calculation of the molecular refractions of amides. The observed differences go far beyond the limits of possible experimental error and show a distinct dependence on the structure. For the tertiary amides (VI) they are negative, being on the average for the D line −0.19, for tertiary formamides (V) they are positive (+ 0.11), while for the secondary amides HCONR'H and RCONR'H they are even more positive (+ 0.30). The difference for the molecular refraction of formamide is even greater when calculated by this scheme. Consequently, it is necessary to introduce at least three new bond refraction values into the different types of amides, i.e., more supplementary constants than are found in the atomic and group refraction systems. Being simpler and more convenient when applied to certain groups of compounds, the system of bond refractions can prove to be more cumbersome and complicated for other classes.

It should be emphasized that the effect of the observed structural influences on the molecular refractions of amides as being only the result of changing the refraction of the C−N bond in the amido group is purely conditional. With equal basis and success it would be possible to refer the variations in the molecular refraction to changes

* It should be borne in mind that the calculation of molecular refractions, according to Vogel [5, 6], assumes the use of the contemporary atomic weight for carbon C = 12.01, while in the system of Eisenlohr [2, 3] the value for carbon is taken as C = 12.00.

TABLE 4

Atomic and Group Refractions and Bond Refractions of Nitrogen in Secondary and Tertiary Carboxylic Acid Amides

Constants	Spectral lines		
	C	D	F
Atomic refractions of nitrogen (according to the Eisenlohr system [2, 3]:			
in secondary amides, and also tertiary formamides	2.729	2.750	2.834
in tertiary amides (other than formamides)	2.491	2.508	2.598
Group refractions (according to the Vogel system [5]):			
HCON< (formamides) and −CONH− (secondary amides)	8.501	8.572	8.732
−CON< (tertiary amides, other than formamides)	7.196	7.261	7.422
Refractions of the C−N bond in the amido group −CON< (according to the system of Vogel and coworkers [6]):			
in secondary amides	1.87	1.88	1.99
in tertiary formamides	1.68	1.68	1.79
in tertiary amides (other than formamides)	1.40	1.38	1.52

TABLE 5

Physical Properties of Carboxylic Acid Amides

Amide	B.p. at pressure (in mm)		d_4^{20}	n_D^{20}	n_C^{20}	Δ_{FC}^{20}	ω_{FCD}^{20}	Amt. of salt and acid impurities (in mole %)
Formamide	103.5-104.5	(9)	1.1336	1.4481	1.4448	115.2	25.71	0.15
Methylformamide	111-111.2	(40)	1.0027	1.4319	1.4291	103.1	23.87	0.3
Dimethylformamide	152.3	(750)	0.9486	1.4304	1.4276	100.9	23.44	0.1
Ethylformamide	109.5-109.7	(30)	0.9552	1.4320	1.4292	98.6	22.82	0.2
Diethylformamide	178.3-178.5	(764)	0.9057	1.4346	1.4320	94.0	21.63	0.05
n-Butylformamide	146-146.2	(49)	0.9128	1.4412	1.4384	93.5	21.19	0.2
Dimethylacetamide	166-167	(767)	0.9437	1.4384	1.4357	97.2	22.17	0.3
Ethylacetamide	109.5-110.5	(22)	0.9237	1.4338	1.4312	94.4	21.76	0.1
Diethylacetamide	184-184.8	(747)	0.9045	1.4396	1.4371	92.0	20.93	0.15
n-Butylacetamide	137.3-138.3	(25)	0.8994	1.4407	1.4381	90.9	20.63	0.1
Dimethylbutyramide	104.5-104.7	(50)	0.9102	1.4428	1.4402	92.3	20.84	0.1
n-Butylbutyramide	142	(16)	0.8828	1.4436	1.4411	88.2	19.88	0.1
Di-n-butylbutyramide	155-155.5	(30)	0.8707	1.4485	1.4461	87.0	19.40	0.2

in the character of the C=O bond. This calculation limitation is inherent to the bond refraction system itself and is produced by the impossibility, in principle, of determining the properties of individual bonds subjected to the influence of their neighboring bonds, which influence stems from the additive scheme and molecular properties as a whole.

The additions, proposed on the basis of our data, to the existing tables of atomic and bond refractions are summarized in Table 4, while the original experimental data are given in Table 5.

Believing that the tables of refraction constants existing in the literature for establishing the structures of organic compounds [2, 3, 5, 6] are wanting in a critical survey, treatment and unification, we regard their being supplemented with new constants, of diverse type according to the method of calculation, as purely a temporary measure.

EXPERIMENTAL*

Methylamine and dimethylamine were obtained from their pure commercial hydrochlorides by the dropwise addition of concentrated aqueous solutions of these salts to finely ground sodium hydroxide, and were dried over soda lime.

* With the participation of Z. I. Sergeeva.

The ethylamine, n-butylamine and di-n-butylamine were prepared by the reaction of ethyl bromide and n-butyl bromide with an alcoholic ammonia solution [8], and were purified by fractional distillation. Technical diethylamine was purified by drying and distillation.

Dimethylformamide and diethylformamide were prepared by the distillation of concentrated aqueous solutions of the corresponding formates, which in turn were obtained by the saturation of pure 85% formic acid with the amines. The other secondary and tertiary formamides were obtained by the pyrolysis of a mixture of the corresponding amine hydrochloride with an equimolecular amount of sodium formate.

The pyrolysis distillates, obtained as mixtures of amides with acid, amine salts and water, were salted out with potash and distilled; here it was found that the obtained amides contain an appreciable amount of amine salts as impurity, which it was impossible to separate by repeated distillation in a column with an efficiency of 15 theoretical plates.

The salt impurities and their amount can easily be established by titrating a weighed sample (~1 g) in alcohol with alcoholic alkali solution (0.05-0.1 N, from a microburette), using phenolphthalein, or even better thymolphthalein, as indicator.*

For the removal of salt impurities the crude amide was treated with powdered potassium hydroxide (at times an alcoholic solution was used) in an amount calculated on the basis of the titration data and sufficient for salt decomposition.

Then the amides were purified by distillation through a column (15 theoretical plates) at atmospheric pressure, or in vacuum through a column having an efficiency of 12 theoretical plates.

After such purification, the salt and acid impurities usually failed to exceed 0.3 mole %. Further repeated treatment with alkali and distillation can lower the amount of impurities several-fold.

To prepare the tertiary amides of acetic acid by the pyrolysis of the salts proved inconvenient. The dehydration of these salts proceeds slowly, and the distillates contain very little of the amides and a huge amount of the original salts. Consequently, the acetamides were prepared by the reaction of acetyl chloride (pure commercial product) with the free amines in ether solution.

The gaseous amines (methyl- and dimethylamine) were introduced in excess into an ice-cooled solution of acetyl chloride in ten volumes of dry ether. The liquid amines were dissolved in three volumes of ether (ethylamine – in ten volumes) and to the cooled solution there was added dropwise and with constant stirring an ether solution (1:1) of the stoichiometric amount of acid chloride (1 mole for 2 moles of amine).

The copious crystalline precipitate of hydrochlorides that was obtained in the acylation was filtered and washed with ether. The residue after distilling off the ether was analyzed for the amount of acid and salt impurities as indicated above, then mixed with the calculated amount of powdered potassium hydroxide and fractionally distilled.

The amides of butyric acid were synthesized in a completely similar manner from butyrl chloride (b.p. 101.3-102° at 754 mm, d_4^{20} 1.0313, n_D^{20} 1.4136, n_C^{20} 1.4114, Δ_{FC}^{20} 83.8), obtained by the action of phosphorus trichloride on pure butyric acid.

Technical formamide was purified from salt impurities by a three-fold vacuum distillation with alkali.

The yields of the pure products, the constants of which are given in Table 5, were 32.59% for the formamides and 45-74% for the other amides.

The densities were determined with 7-13 ml pyknometers, reduced to zero and accurate to 0.0001.

A regular Pulfrich (Zeiss) refractometer was used for the refractive index measurements. The accuracy of the refractive index readings was ± 0.0001, while the mean dispersion Δ_{FC}^{20} was approximately 4 times greater. For the vast majority of the synthesized amides, the density and refractive index values are communicated accurately for the first time.

SUMMARY

1. Twenty secondary and tertiary amides of monocarboxylic acids were synthesized, the majority of which were obtained in pure form and described in detail for the first time.

* It was shown by N. A. Menshutkin that aliphatic amine salts under these conditions titrate as free acids.

2. It was shown that the molecular refraction of amides depends on their structure and cannot be accurately calculated from one refraction constant, characterizing either the amide nitrogen or the amido group.

3. It was proposed to supplement the existing tables of atomic and group refractions with new constants for the amides of different structure, presented in Table 4.

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PHYSICOCHEMICAL ANALYSIS OF THE TERNARY SYSTEM

UREA – ACETIC ACID – PHENYLACETIC ACID

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The purpose of the present work was to study the ternary system urea–acetic acid–phenylacetic acid by the thermal method, and also to study the electrical conductivity, fusion and viscosity of the binary systems: urea–phenylacetic acid and acetic acid–phenylacetic acid.

A study of the reaction of organic acids, in particular, of acetic and phenylacetic acids with urea is of definite interest from the theoretical standpoint, since it is known that urea behaves as a weak base. Together with this, the study also possesses practical importance, since urea and organic acids can have a mutual use: 1) in the production of urea resins, where, besides urea, organic acids are used as condensing agents; 2) in the mutual use of urea as fertilizer and phenylacetic acid as a growth stimulant, used in grafting for the purpose of accelerating root-formation and increasing the percent of rooted plants.

The study was made by the visual-polythermal method. The temperatures at which the last crystals disappeared were taken as the melting points of the mixtures.

The starting substances were of C.p. quality; their melting points were close to those recorded in the literature [1], and specifically: 132° for urea, 16.6° for acetic acid and 75° for phenylacetic acid.

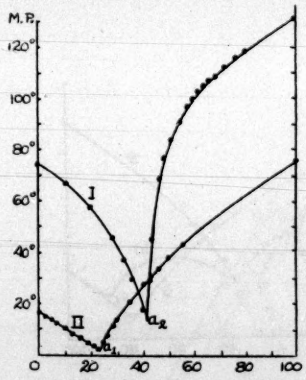

Fig. 1. Fusion curves. I) Phenylacetic acid–urea; II) acetic acid–phenylacetic acid.

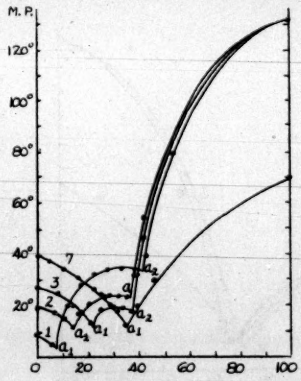

Fig. 2. Curves of the sections 1, 2, 3, 7.

Binary Systems

1) The system urea–acetic acid has been studied by a number of authors [2-4]. All of the investigators established the presence of the compound $CO(NH_2)_2 \cdot 2CH_3COOH$ in the system, which appears as a maximum on the phase-rule diagram. It was also established that this compound is already considerably dissociated at its melting temperatures.

Our checking of this system by the thermal method confirmed the literature data.

2) Compound formation is not revealed in the system urea–phenylacetic acid. The fusion diagram is characterized by a simple eutectic with m.p. 15° at 41 mole % of urea. The data for this system are given in Table 1 and Fig. 1.

3) The system acetic acid–phenylacetic acid is characterized by a simple eutectic with m.p. 2° at 23 mole % of phenylacetic acid. The data for this system are given in Table 1 and Fig. 1.

TABLE 1

Melting Points of Binary Mixtures of Phenylacetic Acid with Urea and Acetic Acid

Phenylacetic acid–urea		Acetic acid–phenylacetic acid		Phenylacetic acid–urea		Acetic acid–phenylacetic acid	
urea (mole %)	m.p.	phenylacetic acid (mole %)	m.p.	urea (mole %)	m.p.	phenylacetic acid (mole %)	m.p.
0.00	74.0°	0.00	16.6°	51.61	84.0°	26.52	7.7°
10.66	67.0	2.27	15.1	54.98	91.0	28.94	11.5
16.46	61.0	4.67	13.6	58.15	97.0	30.60	13.8
20.13	57.9	6.75	12.0	60.19	100.0	35.02	19.8
28.59	46.5	9.94	10.6	62.14	102.0	39.82	26.6
33.22	37.0	12.82	8.7	64.04	105.0	42.89	29.2
36.19	30.0	15.90	7.0	65.88	105.9	46.13	32.6
40.37	18.0	19.19	4.2	69.39	109.2	50.72	37.2
43.05	29.0	21.28	3.3	73.48	112.1	56.96	42.5
46.85	69.0	22.72	2.5	77.27	115.0	–	–
49.30	77.0	24.97	5.2	80.80	118.0	–	–

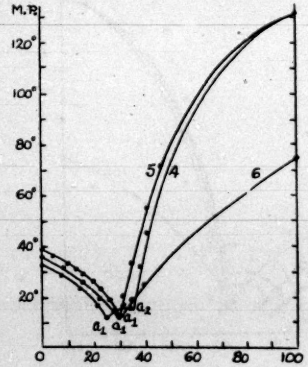

Fig. 3. Curves of the sections 4, 5, 6.

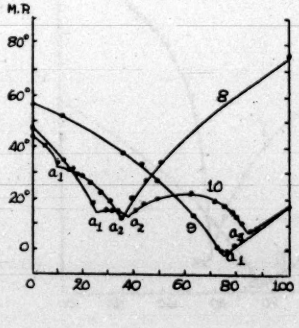

Fig. 4. Curves of the sections 8, 9, 10.

Sections through the ternary system. To develop the crystallization surface of the ternary system a total of 10 sections was studied in the directions shown in Fig. 5. The numbers of the sections correspond to the numbers of the curves in Figs. 2, 3, and 4.

Section 1 (87.18 mole % of acetic acid and 12.82 mole % of phenylacetic acid) intersects (Table 2, Fig. 2) the fields of acetic acid, compound $CO(NH_2)_2 \cdot 2CH_3COOH$ and urea. The intersection points of the branches correspond to: a_1 – 7.5 mole % of urea at 4°, a_2 – 41 mole % of urea at 33°.

Section 2 (64.98 mole % of acetic acid and 35.02 mole % of phenylacetic acid) intersects the same fields (Table 2, Fig. 2), a_1 – 15 mole % of urea at 11°, a_2 – 37 mole % of urea at 23°.

Section 3 (58.15 mole % of acetic acid and 41.85 mole % of phenylacetic acid) intersects the same fields (Table 2, Fig. 2), a_1 – 21 mole % of urea at 12°, a_2 – 37 mole % of urea at 18°.

TABLE 2

Melting Points of the Ternary Mixtures (Sections 1-5)

Section 1		Section 2		Section 3		Section 4		Section 5	
urea (mole %)	m.p.	urea (mole %)	m.p.	urea (mole %)	m.p.	urea (mole %)	m.p.	urea (mole %)	m.p.
0.00	8.7°	0.00	19.5°	0.00	27.5°	0.00	32.5°	0.00	36.0°
5.73	4.9	7.05	17.6	7.45	25.0	7.76	29.2	7.95	32.1
11.43	19.8	11.15	14.5	14.52	19.8	15.08	23.5	15.42	26.5
17.01	28.2	13.82	11.0	17.26	17.5	22.00	16.5	22.47	19.5
22.50	32.3	16.45	17.0	21.26	13.0	25.97	12.0	26.11	16.0
27.91	34.2	20.30	20.6	25.14	18.9	28.55	15.5	29.10	12.5
33.33	34.7	26.52	23.5	30.14	19.7	32.00	16.9	31.73	20.2
38.48	33.8	28.93	23.4	33.77	19.1	34.75	15.8	35.37	33.5
43.64	38.2	32.48	23.2	37.30	17.8	38.33	32.0	41.31	55.1
48.74	45.0	35.95	23.0	39.62	37.0	40.65	45.1	46.93	72.2
53.74	79.0	38.22	32.2	41.86	46.5	–	–	–	–
–	–	43.73	54.0	–	–	–	–	–	–

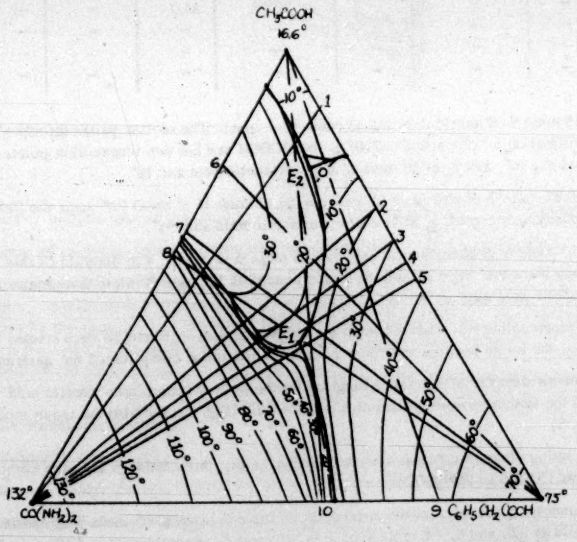

Fig. 5. Fusion diagram of the ternary system urea–acetic acid–phenylacetic acid.

Section 4 (52.75 mole % of acetic acid and 47.25 mole % of phenylacetic acid) intersects the same fields (Table 2, Fig. 3), a_1 – 26 mole % of urea at 12°, a_2 – 36 mole % of urea at 15°.

Section 5 (49.27 mole % of acetic acid and 50.73 mole % of phenylacetic acid) intersects the fields (Table 2, Fig. 3) of urea and phenylacetic acid. The branches intersect in the point a_1 at 30 mole % of urea and 12°.

Section 6 (75 mole % of acetic acid and 25 mole % of urea) intersects the fields (Table 3, Fig. 3) of phenylacetic acid and compound $(NH_2)CO \cdot 2CH_3COOH$, a_1 at 35 mole % of phenylacetic acid and 11.5°.

Section 7 (60 mole % of acetic acid and 40 mole % of urea) intersects the same fields (Table 3, Fig. 2), a_1 at 31 mole % of phenylacetic acid and 12°.

TABLE 3

Melting Points of the Ternary Mixtures (Sections 6-10)

Section 6		Section 7		Section 8		Section 9		Section 10	
phenylacetic acid (mole %)	m.p.	phenylacetic acid (mole %)	m.p.	phenylacetic acid (mole %)	m.p.	acetic acid (mole %)	m.p.	acetic acid (mole %)	m.p.
0.00	39.3°	0.00	40.0°	0.00	44.0°	0.00	57.0°	0.00	48.0°
4.68	36.4	4.68	37.5	4.68	40.0	12.00	52.0	12.11	34.0
9.96	32.9	9.96	34.7	9.96	33.5	35.61	37.0	14.50	31.0
12.82	31.0	12.82	31.0	12.82	32.5	41.85	33.0	23.90	17.0
15.90	28.7	15.90	26.5	15.90	31.1	48.99	27.3	30.69	15.0
19.19	26.0	19.19	24.5	17.91	29.2	62.92	13.7	32.11	15.0
22.72	23.5	22.72	22.2	19.19	28.0	73.26	0.0	34.83	14.5
26.51	19.9	26.51	21.0	22.72	25.0	74.05	−0.5	41.51	15.0
30.61	12.0	30.61	18.0	26.65	21.8	76.56	−0.5	44.05	17.0
35.03	18.5	35.03	11.5	30.61	18.0	79.22	1.0	48.74	19.0
39.82	25.2	39.82	20.0	33.22	15.0	81.56	3.0	61.89	21.5
–	–	46.17	30.1	35.03	12.0	–	–	72.02	19.0
–	–	–	–	39.82	19.5	–	–	75.51	17.0
–	–	–	–	45.03	26.9	–	–	78.51	14.5
–	–	–	–	50.72	34.1	–	–	80.29	13.5
–	–	–	–	–	–	–	–	82.15	10.0
–	–	–	–	–	–	–	–	85.50	7.0
–	–	–	–	–	–	–	–	87.21	7.5

Section 8 (55 mole % of acetic acid and 45 mole % of urea). The section passes through (Table 3, Fig. 4) the region of crystallization for compound $CO(NH_2)_2 \cdot 2CH_3COOH$ and has two intersection points: a_1 at 11 mole % of phenylacetic acid and 32°, and a_2 at 36 mole % of phenylacetic acid and 12°.

Section 9 (79.87 mole % of phenylacetic acid and 20.13 mole % of urea) intersects the fields (Table 3, Fig. 4) of acetic acid and phenylacetic acid, a_1 at 75 mole % of acetic acid and −1°.

Section 10 (57 mole % of phenylacetic acid and 43 mole % of urea). The diagram (Table 3, Fig. 4) consists of four crystallization branches: a_1 − 25 mole % of acetic acid at 14°, a_2 − 38 mole % of acetic acid at 12° and a_3 − 84 mole % of acetic acid at 6°.

Fairly strong supercooling was observed when the sections 3, 4, 5, 7, 8 and 10 were studied in the region of the eutectic point E_1, the liquid became viscous and occluded air, which complicated the determinations.

On the basis of our data the planar fusion diagram for the ternary system urea−acetic acid−phenylacetic acid was constructed and the isotherms were plotted at intervals of 10° (Fig. 5), and also the space model of the diagram was constructed (Fig. 6).

The obtained fusion diagram contains 4 crystallization fields: three fields of the pure components and one field of the compound $CO(NH_2)_2 \cdot 2CH_3COOH$.

Two ternary etuectic points exist in the system: E_1 30 mole % of urea, 35 mole % of acetic acid and 35 mole % of phenylacetic acid at 12°, and E_2 − 8 mole % of urea, 74 mole % of acetic acid and 18 mole % of phenylacetic acid at −3°.

We also studied the electrical conductivity, viscosity and density in the binary systems: urea−phenylacetic acid and acetic acid−phenylacetic acid. The obtained curves have a gentle, almost straight-line character, which indicates the absence of chemical reaction between the components in the liquid phase.

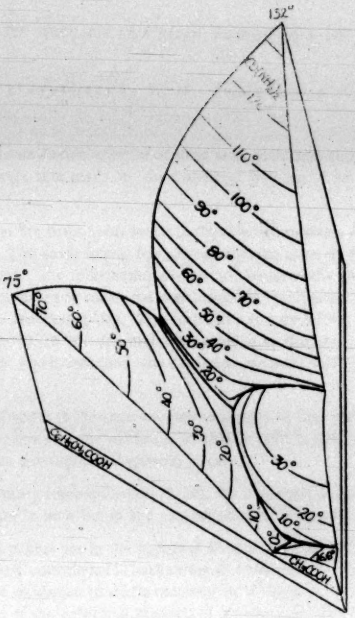

Fig. 6. Space model of the ternary system urea–acetic acid–phenylacetic acid.

SUMMARY

1. The thermal analysis method was used to study the system: urea–acetic acid–phenylacetic acid.

2. The absence of chemical union between urea and phenylacetic acid was established.

3. The dimensions of the crystallization fields go in hand with the melting points of the corresponding compounds. The largest crystallization field belongs to urea, being the highest melting, followed by the phenylacetic acid field, and then by the field of the compound $CO(NH_2)_2 \cdot 2CH_3COOH$ with m.p. 39°. An extremely small crystallization field is possessed by the acetic acid.

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STUDY OF THE OXIDATION PRODUCTS OF RESIN ACIDS

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A systematic study of the oxidation kinetics of solid resin acids and also a study of the influence of different factors on the oxidation rate were first made in the Chemical Institute of the Academy of Sciences of Byelorussian SSR [1-3].

The studies revealed that the resin acids found in the crystalline state, and also their salts, are oxidized by oxygen at an increasing rate. The acids found, from X-ray analysis data, in the amphorous condition suffer maximum oxidation right at the start. The relationship established between the character of the kinetics curves and the nature of the solid phase permitted us to make the conclusion that increasing reaction rate is first of all a function of the crystalline nature of the reacting solids. The activation energy for the oxidation of resin acids in the crystalline state is of the order of 12,000-15,000 cal/mole. Depending on the conditions under which the acids are obtained and on the experimental conditions used, the oxidation proceeds both in the kinetic and in the diffusion region.

A number of papers by Dupont [4-7] were devoted to a study of the oxidation of abietic acid in solution. The character of the kinetics curves for the oxidation of abietic acid in solutions is similar to that of the curves for the oxidation of hydrocarbons in the liquid and gaseous phases.

In accord with contemporary representations [8-10], the oxidation of organic substances in solutions by oxygen proceeds by a chain mechanism in both liquid and gaseous phases. Free radicals appear as the chain carriers.

In neither our published papers nor in the papers of Dupont were the oxidation products of resin acids studied. In a paper by D. Tishchenko and coworkers [11] appearing in 1950 there is given on the basis of elementary analysis data the composition of the oxidation products obtained from fir pitch, being oxidized under natural, constantly changing, conditions, and also of the oxidation products of abietic acid, and a scheme for the oxidation is proposed.

The present work is devoted to a study of the oxidation products of abietic acid and the crystalline portion of pitch.

EXPERIMENTAL

To study the oxidation products of resin acids there was taken the product obtained by the oxidation of abietic acid, the melting point of which in a sealed capillary was 172° and $[\alpha] = -105°$, with oxygen at 60°, and the crystalline portion of pitch, recrystallized from acetone and oxidized with oxygen in a vacuum apparatus at 50°. In addition to studying the samples oxidized under the indicated conditions, an experiment was made with abietic acid and the crystalline portion of pitch in which these two products were oxidized with atmospheric oxygen at room temperature for a period of 3 years.

In the oxidation products of the resin acids were determined the number of double bonds (before and after oxidation), peroxides, hydroxyl and carboxyl groups.

The double bonds were determined by three methods: acetyl hydroperoxide, method of Hubl-Waller and method of Margosches. A sample of abietic acid weighing 0.12 g was dissolved in 10 ml of chloroform. To the solution was added acetyl hydroperoxide in 2-3 times the amount needed for the addition of oxygen to the double bonds. After 24 hours to the solution was added 10 ml of 10% KI solution and 10 ml of acetic acid and the amount of hydroperoxide determined. The results of the double bond determinations for the oxidized and unoxidized resin acids are given in Table 1.

A reduction in half of the number of double bonds in the resin acid oxidation products indicates that in the oxidation the addition of the oxygen proceeds only at the conjugated double bonds.

According to literature data, the oxidation of organic compounds at low temperatures proceeds with the formation of peroxides and, in particular, of hydroperoxides. The peroxides are determined by the stannate and potassium iodide methods.

TABLE 1

Acid	Number of double bonds found in the acid		
	with acetyl hydroperoxide	Nargoschey's method	Hubl-Waller method
Unoxidized abietic acid	1.92	1.93	1.88
Oxidized abietic acid	1.1	1.06	–
Solid portion of pitch	–	1.67	1.8
Oxidized solid portion of pitch	–	0.68	0.85

A weighed sample of the oxidized resin acid was dissolved in 20 ml of acetic acid. The air in the flask was displaced by carbon dioxide gas, after which was added 10 ml of 10% KI solution and 10 ml of standard $SnCl_2$ solution. After standing for 3 hours the excess $SnCl_2$ was back-titrated with I_2 solution. By the potassium iodide method the evolved iodine after standing for 3 hours was back-titrated with sodium thiosulfate. The last method has the disadvantage that the evolved iodine can partially add to the double bond of the oxidized acid, which leads to lowered results for the amount of peroxides.

In Table 2 are given the data on the amount of peroxides obtained by the stannate method.

TABLE 2

Acid	Oxidation conditions	No. of active oxygen atoms in 1 acid molecule
Crystalline portion of pitch	In the laboratory to the air for 3 years	0.45-0.52
Abietic acid	In the laboratory to the air for 3 years	0.2-0.3
Abietic acid	Oxidized with oxygen at 60°	0.033

In the oxidized crystalline portion of the pitch about 20-25% of the combined oxygen is found in the active state, and for the abietic acid, oxidized with oxygen in the apparatus at 60°, about 1%.

If the oxygen adds with the formation of hydroperoxides, then the latter on decomposition can give alcohols. We determined the alcohol groups by acetylation. The determination results are given in Table 3.

TABLE 3

Acid	Oxidation conditions	No. of OH groups in 1 acid molecule
Abietic acid	Oxidized with oxygen in the apparatus at 60°	1.01
Abietic acid	Unoxidized	0.05
Crystalline portion of pitch	Unoxidized	0.19
Crystalline portion of pitch	Oxidized with oxygen at 50°	1.98
Abietic acid	In the laboratory to the air for 3 years	2.43

From the presented data it follows that alcohols are one of the reaction products obtained in the oxidation of resin acids. However, the amount of combined oxygen is approximately twice the amount of oxygen found in the alcohol groups.

It was of interest to determine the ability of resin acids to be oxidized by oxygen after their oxidation with acetyl hydroperoxide. To 10 g of purified abietic acid dissolved in 200 ml of alcohol was added 7 ml of 88.1% acetyl hydroperoxide. After 5 days 2.04 g-atoms of oxygen was added to the acid molecule. On dilution with water a white sticky mass deposited, which was washed with water several times and vacuum dried at 20-25°, after which it had m.p. 106-107° in a sealed capillary.

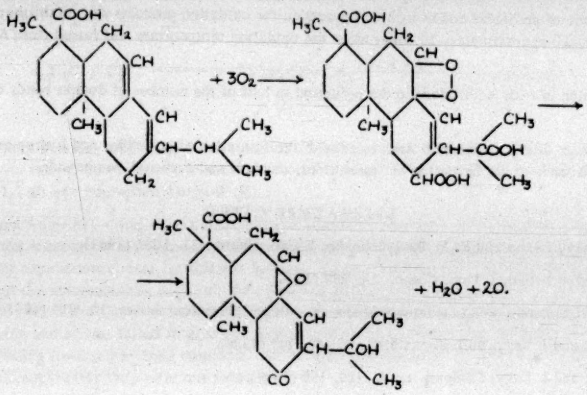
The product failed to crystallize from the organic solvents investigated by us and on removing the solvent solidified into a glassy mass. To the crystalline portion of pitch under the same conditions of oxidation with acetyl hydroperoxide there added 1.97 g-atoms of oxygen.

The abietic acid and the crystalline portion of pitch, which had been oxidized with acetyl hydroperoxide, were then oxidized in the vacuum apparatus with oxygen at 720 mm and 60°. The absorption of oxygen could not be detected after 17 hours of oxidation, whereas the abietic acid, not oxidized with acetyl hydroperoxide, in the same time at 50° and the same pressure absorbed 7 ml of oxygen, while the crystalline portion of pitch absorbed 9.4 ml. Such a behavior for the acids can be due either to the fact that the oxygen adds at the double bond (and since in the oxidation with acetyl hydroperoxide the oxygen has already been added the molecular oxygen fails to add) or to a reduction in the reactivity of the C–H bonds, at which the addition of oxygen takes place, as the result of oxygen addition to the double bond.

The absorption maximum for abietic acid is found at 2410 A, and for the unoxidized crystalline pitch portion at 2500 A. On oxidation the absorption coefficient at the maximum is reduced, while in the long-wave portion of the spectrum it is increased to such a degree that the oxidation products are colored by atmospheric oxygen.

DISCUSSION OF RESULTS

The obtained experimental data permit giving the following scheme as being the most probable for the oxidation of resin acids with oxygen:



The first stage of the oxidation, as we showed earlier, is the adsorption of oxygen by the resin acids. The adsorbed oxygen either adds to one of the double bonds present in the molecule with the formation of the peroxide, which is unstable and decomposes to the oxide, or enters between the carbon and hydrogen of the C—H bond, rupturing it. The number of such bonds, found in the alpha-position, in the abietic acid molecule, as can be seen from the scheme, is equal to four. The primary reaction products in the latter case should be hydroperoxides.

After the addition of an atom of oxygen to the double bonds, as the experimental data on the oxidation of the resin acids with oxygen show, the acids oxidized with acetyl hydroperoxide lose their extreme reactivity and practically fail to be oxidized by oxygen. Consequently, if the oxygen adds to one of the double bonds, then the oxidation of the two C—H bonds, found in the alpha-position to this double bond, will not occur. There remain two other C—H bonds, found in the alpha-position to a double bond, one of which contains a tertiary carbon atom. The products of oxygen insertion are hydroperoxides. According to the literature [10], secondary hydroperoxides decompose with the formation of carbonyl compounds. Tertiary hydroperoxides decompose with the evolution of atomic oxygen, oxidizing the side chains, which leads to the formation of volatile organic compounds, observed by us in the oxidation of the resin acids.

The amount of oxygen, absorbed from the gas phase in the oxidation of the acid molecule, according to this scheme should be equal to four atoms. Three of them are bound with the acid and one of them with H_2O, which was actually established by us [2]. If the oxygen entered between the carbon and the hydrogen of all of the C—H bonds found in the alpha-position, and the double bonds remained untouched, then four molecules of oxygen should be added to the acid molecule. In not one of the experiments was this amount of oxygen added to the acid.

The presence of three conjugated chromophore groups —CO, C=C and , causes a shift in the absorption spectrum for abietic acid in the long-wave region to such a degree that the absorption also embraces part of the visible light region, which explains the bright yellow color of the resin acid oxidation products.

We also do not exclude the possibility that the first stage of the oxidation can be the insertion of the oxygen molecule between carbon and hydrogen, leading to the formation of hydroperoxides. Benzoyl and acetyl hydroperoxides, as was shown [2, 12], oxidize one of the double bonds in abietic acid in a matter of a few minutes, whereas the addition of an atom of oxygen to the second bond takes several days. The hydroperoxide formed in the reaction can oxidize one of the double bonds, which leads to the reduction in half of the number of double bonds in the molecule.

SUMMARY

1. A study was made of the products obtained in the oxidation of abietic acid and the crystalline portion of pitch with oxygen in a vacuum apparatus at 50-60° and with air at room temperature.

2. The presence of peroxides and of hydroxyl groups in the oxidation products was established. The amount of peroxides was reduced approximately 10 times when the oxidation temperature was raised from room temperature to 60°.

3. The oxidation of resin acids leads to the reduction in half of the number of double bonds in the acid molecule.

4. The first stage of the oxidation is associated with the formation of peroxides and hydroperoxides, the decomposition of which leads to the formation of monoxides, alcohols and carbonyl compounds.

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* See Consultants Bureau Translation, page 1271.

CONDENSATION OF ACETYLENE WITH CHLOROBENZENE

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Continuing the study of the alkylation of the aromatic ring with acetylene [1], we studied its condensation with chlorobenzene. In accord with our earlier obtained results the following scheme for this condensation can be expected:

$$C_6H_5Cl + C_2H_2 \longrightarrow ClC_6H_4CH{=}CH_2 \xrightarrow{+\,C_6H_5Cl} (ClC_6H_4)_2CHCH_3.$$

(I) (II)

Cook and Chambers [2], who studied the condensation of acetylene with benzene and its homologs, also described the reaction with chlorobenzene; in this connection they were able to obtain a small amount of an oily substance, taken as 1,1-di-(4-chlorophenyl)ethane (II).

Boeseken and Adler [3], using an extremely active aluminum chloride, obtained a tar and a small amount of viscous oil from the reaction of acetylene with chlorobenzene, which were regarded as being chlorostyrene polymers, although sufficient experimental data for this was lacking. Latter Grummit and coworkers [4] synthesized the p,p'-isomer (II) through the corresponding carbinol; the substance proved to be crystalline (m.p. 54-55°). The attempts of these authors to obtain the same crystalline product by the condensation of chlorobenzene with acetaldehyde, ethlylidene chloride and acetal failed to give the desired result. In all cases small amounts of fluorescent oils were obtained, not differing from (II) in their constants. All of these substances on oxidation gave p,p'-dichlorobenzophenone; however, apparently they were not pure.

For the condensations we passed acetylene into a large excess of chlorobenzene, mixed with $AlCl_3$. Having studied the influence of the reactant ratios, amount of $AlCl_3$, temperature and reaction time, we found that the best results are obtained when the reaction is run for 2 hours at 80° with 0.08 mole of $AlCl_3$ per mole of acetylene and using 1 liter of chlorobenzene for 0.5 mole of acetylene. An increase in the amount of $AlCl_3$ leads to the accumulation of tar.

The basic condensation product is an oil with constants corresponding to those of (II). When the oil was oxidized with chromic anhydride we constantly obtained only p,p'-dichlorobenzophenone and p-chlorobenzoic acid. The yield of the basic condensation product was as high as 77% of theory. In addition to (II) there were also isolated small amounts of two low-boiling fractions. One of them, vigorously decolorizing bromine, is apparently a mixture of o- and p-chlorostyrenes (I), while the other is a mixture of o- and p-chloroethylbenzenes.

As a result, the condensation products from acetylene and chlorobenzene are similar to those obtained in the reactions of acetylene with benzene and other aromatic compounds. The chlorostyrenes (I) formed in the first stage react with the excess chlorobenzene, giving 1,1-di-(chlorophenyl)ethane (II); part of the chlorostyrenes are reduced to chloroethylbenzenes, apparently as the result of the high molecular tarry substances being dehydrogenated. Later we studied* the chlorination of (II), which permitted us to establish the structure of the isomeric 1,1-di-(chlorophenyl)ethanes.

The chlorination was run with illumination at 100-120° in the presence of small amounts of PCl_5. The oily chlorination product was vacuum distilled. In accord with our data on the chlorination of 1,1-diphenylethane [5] we expected the following reaction:

$$(ClC_6H_4)_2CHCH_3 \xrightarrow{+\,Cl_2} (ClC_6H_4)_2CClCHCl_2 \xrightarrow{-HCl} (ClC_6H_4)_2C{=}CCl_2.$$

The oil partially crystallized after distillation. Oxidation of the isolated crystals gave 2,4'-dichlorobenzophenone. Oxidation of the residual oil gave 4,4'-dichlorobenzophenone. These data show that the 1.1-di-(chlorophenyl)-2,2-dichloroethylene (II) is a mixture of the o,p'- and p,p'-isomers.

* N. P. Epifanova participated in this portion of the work.

As a result, the basic condensation product of acetylene with chlorobenzene (II) proved to be a mixture of the o,p'- and p,p'-isomers of 1,1-di-(chlorophenyl)ethanes. Judging from the yields of chlorination products, the isomers are present in approximately equal amounts.

The formation of the indicated mixture of isomers agrees with the literature relative to the composition of technical DDT and similar substances [6]; in our case the amount of the o,p'-isomer is unusually great.

EXPERIMENTAL

The condensation of acetylene with chlorobenzene was made in a liter Erlenmeyer flask, fitted with a mechanical stirrer and a sleeve dipping into the reaction mixture, thus creating a seal; in addition, the flask was fitted with a thermometer and tubes for the introduction of acetylene and $AlCl_3$, and for the escape of unreacted acetylene. The acetylene was admitted from a gasometer, first passing through two wash bottles with chromic mixture and a column filled with calcium chloride. The escaping acetylene was collected in a second gasometer. Below is given a description of one of the experiments, giving maximum yields of 1,1-di-(chlorophenyl)ethane (II).

Into 1 liter of chlorobenzene, heated to 80°, with vigorous stirring was introduced 10 g (0.08 mole) of finely divided $AlCl_3$. Acetylene was passed at a rate of 9 liters per hour; at first it was almost completely absorbed. After 1.5 hours the absorption was noticeably diminished and the reaction was terminated. About 11.5 liters (0.5 mole) of the acetylene reacted. The mixture was poured into cold water that had been acidified. The chlorobenzene solution was separated, washed with water, and dried over calcium chloride. Distillation at atmospheric pressure gave: chlorobenzene 912 ml, fraction with b.p. 140-200°, 6.7 g, fraction with b.p. 200-250°, 2 2 g. The residue was vacuum distilled. There were obtained: 1,1-di-(chlorophenyl)ethane (II) with b.p. 173-183° at 8 mm, 84 g (77% of the theoretical based on reacted chlorobenzene); fraction 200-250° at 8 mm, 10.7 g; undistillable tars 7.5 g.

Repeated distillation of the first fraction gave a substance with b.p. 173-177° (730 mm), n_D^{18} 1.5260, d_4^{18} 1.0505. These data are close to the constants for the o- and p-chloroethylbenzenes [7]. Oxidation of the fraction with chromic anhydride in glacial acetic acid gave a mixture of acids. Boiling water extracted o-chlorobenzoic acid with m.p. 140°, while recrystallization of the residue from alcohol gave p-chlorobenzoic acid with m.p. 242°. Both acids, isolated in equal amounts, failed to depress the melting point when mixed with the corresponding authentic compounds.

The second fraction decolorized bromine solution; on distillation it gave a small amount of liquid with b.p. 225-230° (730 mm), n_D^{17} 1.5750, d_4^{17} 1.1138. Apparently this fraction is a mixture of o- and p-chlorostyrenes [8].

1,1-Di-(chlorophenyl)ethane (II) is a colorless, slightly fluorescent oil, b.p. 163-165° at 7 mm, n_D^{18} 1.5318, d_4^{18} 1.0943.

Oxidation. Twenty grams of (II) was boiled for 6 hours with 80 g of chromic anhydride and 250 ml of glacial acetic acid. The mixture was poured into water, the obtained precipitate filtered, dissolved in ether, washed with soda, and after removal of the ether, recrystallized from ligroin. About 13 g of 4,4'-dichlorobenzophenone was obtained with m.p. 139-140° [9]. The mixed melting point with the known compound failed to be depressed.

Acidification of the soda extracts gave a small amount of p-chlorobenzoic acid with m.p. 242°.

Chlorination. To 20.2 g of (II) was added 0.1 g of PCl_5 and a stream of dry chlorine was passed for 6 hours at 100-120° with illumination by a 200 W lamp. The weight increase was 8.7 g, which corresponds to the introduction of 3 atoms of chlorine. The ether solution of the chlorination product was washed with weak alkali, water, and then dried over calcium chloride. The oil remaining after distilling off the ether was vacuum distilled. There was obtained 17 g of a fraction with b.p. 225-230° at 30 mm. The strong evolution of HCl was noted during distillation. The obtained fraction was again dissolved in ether and washed with soda. The oil became crystalline after removal of the ether. About 8 g of crystals was obtained with m.p. 77-78° (from alcohol), being 1,1-di-(2,4'-chlorophenyl)-2,2-dichloroethylene (III) [6].

0.1942, 0.2497 g sub.: 0.3502, 0.4464 g AgCl. Found %: Cl 44.32, 44.25. $C_{14}H_8Cl_4$. Calculated %: Cl 44.59.

The oxidation of (III) with chromic anhydride gave 2,4'-dichlorobenzophenone with m.p. 66° [10].

The oily chlorination product, remaining after the removal of (III), was also oxidized with chromic anhydride. Only 4,4'-dichlorobenzophenone was obtained with m.p. 139-140°.

SUMMARY

1. The condensation of a large excess of chlorobenzene with acetylene in the presence of $AlCl_3$ gave 1,1-di-(chlorophenyl)ethane in a yield of 77% of the theoretical. In addition, small amounts of the o- and p-isomer mixtures of chloroethylbenzene and chlorostyrene were isolated.

2. By chlorination and oxidation it was proven that the obtained 1,1-di-(chlorophenyl)ethane is a mixture of o,p'- and p,p'-isomers.

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THE INFLUENCE OF ULTRAVIOLET IRRADIATION ON ORGANOMAGNESIUM COMPOUNDS

M. S. Malinovsky and A. A. Yavorovsky

Beginning with 1949 G. A. Razuvaev and coworkers have been making a detailed study of the photoreactions of organometallic compounds in different solvents, in particular of mercury, proceeding with the formation of free radicals [1]. It appeared of interest to us to also make a study of the behavior of organomagnesium compounds under ultraviolet irradiation, all the more so since it had hardly been studied. In the literature it is indicated by Gilman [2] that tert-butylmagnesium chloride and isobutylmagnesium bromide are not affected by ultraviolet irradiation. In another paper by Lichtenwalter [3] mention is made in a cursory manner that the formation of organomagnesium compounds can be accelerated by either photochemical means or by exposure to the influence of certain metal salts. However, the author fails to give any indications as to the type of illumination used, or as to the yields of the organomagnesium compounds.

It appeared to us that the question of the behavior of organomagnesium compounds when exposed to ultraviolet irradiation deserves much consideration, since such a study can assist in probing deeper into the mechanism of Grignard reactions, and also into the structure of organomagnesium compounds. With this purpose in mind we undertook the present study, dividing our efforts in three directions, namely:

1) the influence of ultraviolet irradiation on the formation of organomagnesium compounds was studied in both ether and benzene media;

2) the influence of ultraviolet irradiation on finished organomagnesium compounds was studied;

3) the influence of ultraviolet irradiation on the reaction between organomagnesium compounds and hydrocarbon halides was studied.

As was to be expected, sufficiently intense ultraviolet irradiation exerts an influence on the formation of organomagnesium compounds, and also on the finished Grignard complexes.

The results of studying the influence of ultraviolet irradiation on the formation of organomagnesium compounds are summarized in Table 1.

TABLE 1

Influence of Ultraviolet Irradiation on the Synthesis of Organomagnesium Compounds in Ether and Benzene Media

Expt. No.	Halide taken formula	Wt. (g)	Medium used for the reaction	Control experiments: yield of RMgX (%)	Control experiments: residual magnesium (%)	Experiments with irradiation: yield of RMgX (%)	Experiments with irradiation: residual magnesium (%)	Difference in yields (%)
1	C_2H_5Br	10.8	Ether	81.4	8.75	90.2	6.0	+ 8.7
2	iso-C_3H_7Br. . . .	12.3		79.2	11.30	74.7	15.4	− 4.5
3	n-C_4H_9Br.	13.7		82.4	8.78	95.8	3.04	+ 13.4
4	iso-C_4H_9Br. . . .	13.7		77.2	12.1	71.2	15.0	− 6.0
5	sec-C_4H_9Br. . . .	13.7		72.0	15.0	62.6	22.0	− 9.4
6	C_6H_5Br	15.7		83.0	9.1	88.0	7.1	+ 5.0
7	$C_6H_5CH_2Br$. . . .	12.7		88.0	5.95	87.5	6.7	− 0.5
8	iso-C_3H_7I. . . .	34.0	Benzene	73.4	12.9	63.2	19.5	−11.1
9	iso-C_4H_9I	36.8		71.3	14.1	59.2	20.4	−12.1
10	iso-$C_5H_{11}I$. . . .	39.6		72.0	13.5	57.6	21.0	−14.4

An examination of Table 1 brings out the following. The irradiation unconditionally affects the yield of organomagnesium compounds: the normal primary alkyl halides and bromobenzene give higher yields, while the isoalkyl halides and especially the secondary alkyl bromides give lower yields. As regards $C_6H_5CH_2MgBr$, for it the results possess little indication, since the difference in yield is a total of only 0.5%, i.e., it exists within the limits of experimental error.

The obtained results can be explained best of all with the aid of the free radical mechanism, which can be expressed by the following equations:

$$RX + Mg \longrightarrow R\cdot + MgX\cdot \quad (1)$$

$$R\cdot + MgX\cdot \longrightarrow RMgX \quad (2)$$

$$RX + MgX\cdot \longrightarrow R\cdot + MgX_2 \quad (3)$$

$$2R\cdot \longrightarrow R{-}R \quad (4)$$

Of these equations, for the primary normal halides and bromobenzene Reactions (1) and (2) are most characteristic, while for the branched alkyl halides Reactions (1), (3) and (4) are most characteristic.

If free radicals are formed when the reaction mixture of halide derivative and magnesium is irradiated, then these radicals can also react with the solvent, which, in particular, was observed in the studies of A. D. Petrov [4], Kharasch [5] and Gilman [6]. However, when the reaction is carried out in ether the separation of such products is practically impossible. Taking this into consideration, we carried out the synthesis of organomagnesium compounds in benzene medium by the method of V. V. Chelintsev [7]. Since, according to the data of this author, the reaction proceeds quantitatively in benzene medium only with the isoalkyl iodides, we limited our study to them. As a result, not only were hydrocarbons of the form R–R isolated but also alkylbenzenes (Table 2), the formation of which can be imagined only in accord with Equation (5)

$$C_6H_7 + R\cdot \longrightarrow C_6H_5R + H\cdot \quad (5)$$

The presented experimental data raised the question: does the reduction in the yield of the organomagnesium compound during its synthesis depend on a change in the reaction mechanism or on the decomposition of the already formed magnesium complex? With this question in mind we undertook the irradiation of several finished Grignard complexes. From the data, given in Table 3, it follows that in the irradiation of methyl- and ethylmagnesium bromides the amount of the organomagnesium compound is noticeably reduced, while in the case of n-C_4H_9MgBr and C_6H_5MgBr it remains practically constant. In the first two cases the evolution of gas was observed. For CH_3MgI it is insignificant and consequently, not indicative, while in the case of C_2H_5MgBr a combustible gas was obtained, containing equal amounts of saturated and olefinic hydrocarbons, which indicates the formation of free radicals, suffering decomposition in accord with the equation

$$C_2H_5\cdot + C_2H_5\cdot \longrightarrow C_2H_6 + C_2H_4 \quad (6)$$

A similar mechanism was proposed by Kharasch [8] in his studies on the influence of cobalt salts on the Grignard reaction.

Simultaneous with gas formation there was observed the deposition of a crystalline colorless precipitate. This precipitate (6.5 g) was decomposed with sulfuric acid solution; in this connection ethane (0.032 mole) was evolved. The formation of ethane in the decomposition of the organomagnesium compound with water is thought to proceed in accord with the following equations:

$$C_2H_5MgBR\cdot 2(C_2H_5)_2O + H_2O \longrightarrow C_2H_6 + 2(C_2H_5)_2O + HOMgBr \quad (7)$$

$$(C_2H_5)_2Mg\cdot 2(C_2H_5)_2O + 2H_2O \longrightarrow 2C_2H_6 + 2(C_2H_5)_2O + Mg(OH)_2 \quad (8)$$

From Reaction (7) 0.032 mole of ethane is formed from 7.2 g of the etherate, while by Reaction (8) it is 2.76 g. From this the most probable conclusion is that the indicated precipitate is the crystallized etherate of the mixed organomagnesium compound. The latter is also supported by the fact that the precipitate contains an appreciable amount of halide. As a result, under the influence of ultraviolet irradiation there occurs a reduction in the concentration of the finished organomagnesium compound due to its conversion into the mixed compound. This

was confirmed by determining the amount of $(C_2H_5)_2Mg$ present in the ethylmagnesium bromide solution that had been exposed to ultraviolet irradiation, and the amount present in the control experiment. A considerable reduction in the amount of the finished organomagnesium compound with the total amount of compound remaining constant is also observed in the other experiments, presented in Table 3.

It appears to us that the gas formation and crystallization processes are interconnected. This bond consists in the fact that the transformation

$$RMgR + MgX_2 \longrightarrow 2RMgX \quad (9)$$

bears a free radical character and can be expressed by the equations:

$$RMgR \longrightarrow RMg\cdot + R\cdot \quad (10)$$

$$R\cdot + MgX_2 \longrightarrow RMgX + X\cdot \quad (11)$$

$$RMg\cdot + X\cdot \longrightarrow RMgX \quad (12)$$

However, the free radicals can also dissociate in accord with Equation (6).

The evolution of gases was not observed in the case of $n\text{-}C_4H_9MgBr$ irradiation. This, in our opinion, is explained by the fact that the C_4H_9 radical can react in accord with Equation (4) with the formation, under the experimental conditions, of liquid octane, which fact was noted in the literature by Kharasch [9].

We explain the negative results obtained by Gilman [2] in the irradiation of $(CH_3)_3CMgCl$ and $n\text{-}C_4H_9MgBr$, as being due to the fact that he used a method that failed to give him sufficiently intense irradiation, and in addition, his experiments were of a purely qualitative nature.

Finally, we studied the influence of ultraviolet irradiation on the reaction of Grignard complexes with a series of halides. From the literature it is known [10] that such reaction fails to take place in the majority of cases if the reaction is carried out at the boiling point of ether. This conclusion was also confirmed in our control experiments. However, although in the case of irradiation a certain reduction in the amount of RMgX is observed, i.e., there is coupling in accord with the equations:

$$RMgX + RX \longrightarrow R\cdot + R\cdot + MgX_2 \quad (13)$$

$$R\cdot + R\cdot \longrightarrow R{-}R$$

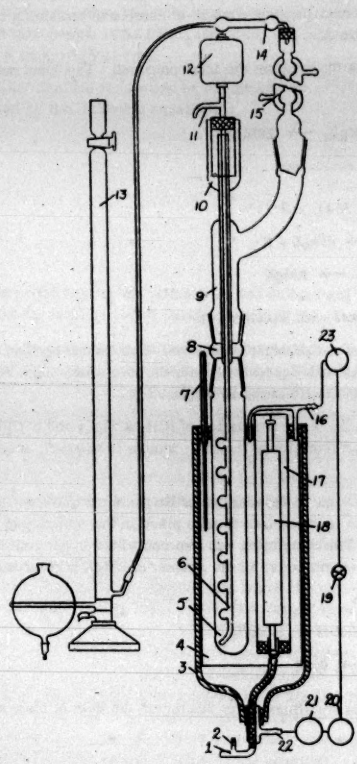
nevertheless, it fails to exceed 5-7% and in general has little significance for this reason the data of these experiments are not presented here.

EXPERIMENTAL

All of the irradiation experiments were run in the specially constructed apparatus shown in the figure.

A PRK-2 mercury quartz lamp served as the light source, operating under overloading (at 220 V, instead of the rated 127 V). In order to avoid the absorption of the ultraviolet light by the salts dissolved in ordinary water, the apparatus was cooled by passing distilled water through it. All of the hydrocarbon halides used for reaction were freshly distilled through a Widmer column. The fractions boiling in a 1° range were taken for the experiments. The purity of the halides was controlled by the boiling points and the refractive indices. The amount of organomagnesium compound formed in the reaction was determined by the method of Gilman [11].

1. Influence of ultraviolet irradiation on the formation of organomagnesium compounds in ether and benzene media. Before starting the experiment the vessel (3) of the apparatus was filled with water, and then the magnesium (Kahlbaum C.p.) was charged into the test tube. All of the apparatus was put into operation and 10-15 ml of anhydrous ether was added through the funnel in the top of the condenser. Then the quartz lamp was turned on and exposure to irradiation maintained for 30 minutes. After this, for initiating the reaction there was added at one time 0.5-1 ml of the starting alkyl halide and the mixture was brought to the boil by reducing the flow rate of the cooling water. Usually the reaction began almost immediately, which was indicated by the characteristic "graying" of the mixture. The boiling was continued for 30 minutes, then the temperature was lowered to 30°, the stirrer put in operation, and the ether solution of the halide derivative added gradually, which addition took 3 hours. Then the mixture was irradiated for 2 hours at 30° and 0.5 hour at the boil, after which the temperature was lowered to 25°, and the volume of the mixture made up to 100 ml with anhydrous ether. The mixture was well-stirred, remaining



Apparatus for the ultraviolet irradiation of organomagnesium compounds. 1) Ozone outlet (to water-jet pump); 2) current lead; 3) protective jacket; 4) reflector; 5) quartz test tube; 6) stirrer; 7) thermometer; 8) coupling; 9) shaped head; 10) mercury seal; 11) spout for sample taking; 12) electric motor; 13) gas buret; 14) calcium chloride tube; 15) reflux condenser; 16) distilled water inlet; 17) quartz tube; 18) PRK-2 quartz lamp; 19) pump; 20) intermediate water reservoir; 21) condenser; 22) water outlet; 23) water pressure reservoir.

under irradiation for 2 hours, after which a 5 ml sample was taken from the upper part of the completely clear solution for analysis. For this purpose hydrogen, admitted through the opening in the top of the condenser, was used to create a slight pressure in the apparatus, causing the solution to rise along the stirrer shaft through the opening found in it into the spout, and then into the test tube graduated to 0.1 ml. After analysis the reaction mixture was decanted from the residual magnesium, the latter was washed with anhydrous ether, then with water, dried, and weighed to 0.01 g.

Parallel with the irradiation experiment, the control experiment without irradiation was run under similar conditions.

For the experiments the quantities used in each experiment were 0.1 mole of halide, 0.1 mole of magnesium and 60 ml of ether.

The experiments with RMgI in benzene medium were run in the above indicated apparatus with charges of 0.2 mole each of magnesium and alkyl halide and 71 ml of benzene. The mixture was irradiated for 1 hour, then with good stirring the catalyst was introduced – freshly distilled dimethylaniline (20 drops). The reaction began at once. The process was run at 20° with constant irradiation for 4 hours. Then the mixture was kept at 70° for 1 hour, cooled to 20°, and to it with stirring was added dropwise ethyl ether in sufficient amount to make the solution completely homogeneous. After 2-hour standing a sample was taken for determination of the total amount of RMgX, while the remaining solution was decanted from the magnesium into an acidified mixture of ice and water. The magnesium, after being treated as indicated above, was weighed. The experimental results are given in Table 1. In the ether layer, after washing it with soda solution, pure water, and drying over calcium chloride, with subsequent removal of the ether and benzene by distillation, was determined the amount of aralkyl hydrocarbons formed. The results are given in Table 2.

The control experiments without irradiation were run in similar manner. In these experiments hydrocarbons of the R–R type were obtained, but no alkylbenzenes.

2. Influence of ultraviolet irradiation on finished organomagnesium compounds. The organomagnesium compounds were obtained in the usual manner from 0.2 mole of RX. After allowing the solution to stand overnight, 100 ml aliquot portions were siphoned into two parallel apparatus: one for irradiation, the other as the control. From each apparatus a sample was taken for analysis, and the first one was irradiated (cooling water circulated at such a rate that the temperature did not exceed $15 \pm 0.2°$). After 1 hour of irradiation the upper part of the condenser was connected through the calcium chloride tube to the gas buret. The experimental results are given in Table 3.

TABLE 2

Expt. No.	Hydrocarbons obtained	Found		Literature data [12]	
		b.p.	n_D^{20}	b.p.	n_D^{20}
1	$C_6H_5C_3H_7$	151°	1.4940	152.5°	1.4932
2	$C_6H_5C_4H_9$	169	1.4955	170.5	1.4957
3	$C_6H_5C_5H_{11}$	197	1.487	198	1.4867

Remarks: The hydrocarbon fractions were isolated by distillation in the microdistillation apparatus [13]. The boiling points were determined by the method of Sivolobov.

TABLE 3

Influence of Ultraviolet Irradiation on Finished Organomagnesium Compounds

Expt. No.	Organomagnesium compound	Control experiments		Experiments with irradiation					Change in composition	
		gram-equivalents per 100 ml		time (hrs)	gram-equivalents per 100 ml		amt. of evolved gas (ml)	external appearance	total amt. RMgX + R_2Mg	R_2Mg
		RMgX	R_2Mg		RMgX	R_2Mg				
1	CH_3MgI	0.125	0.006	28	0.12	0.003	16	Without change	−4	−50
2	C_2H_5MgBr	0.215	0.14	64	0.202	0.082	470	A precipitate deposits for 15 hours	−6.5	−41
3	n-C_4H_9MgBr. . .	0.162	0.12	80	0.160	0.070	−	Separation into layers	−	−35
4	C_6H_5MgBr	0.180	0.125	80	0.178	0.100	−	Turbid	−	−14

In the irradiation of CH_3MgI the evolution of gas was observed only in the beginning. The gas was not analyzed. In the irradiation of C_2H_5MgBr there was obtained 470 ml of combustible gas, in 50 ml of which there was found C_nH_{2n} 10 ml, C_nH_{2n+2} 10 ml, oxygen 6 ml, nitrogen 23 ml.

The obtained crystalline precipitate (see above) was washed with anhydrous ether and dried in a steam of hydrogen at 35°. There was obtained 6.5 g of precipitate, the decomposition of which with a cold solution of sulfuric acid gave 790 ml of a combustible gas (22°, 745 mm), or 716 ml (0.032 mole) under standard conditions. This gas proved to be ethane. The water from the decomposition of the precipitate gave a copious precipitate of silver halide when treated with a solution of silver nitrate.

In both the control and irradiation experiments not only was the amount of RMgX determined, but also the amount of R_2Mg, using the method developed by Schlenk and made accurate by Noller [14].

SUMMARY

1. The influence of ultraviolet irradiation on the formation of organomagnesium compounds was studied.

2. The postulation was expressed that the reaction of alkyl halides with magnesium under ultraviolet irradiation is of free radical nature.

3. The formation of free radicals under the conditions of irradiation of finished organomagnesium compounds was demonstrated.

4. An apparatus was constructed for running the experiments under ultraviolet irradiation, in which the maximum irradiation intensity was assured under any temperature regime in the limits from 10 to 90°.

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ACTION OF ULTRASONICS ON CARBOHYDRATE SOLUTIONS

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In connection with the studies on elucidating the influence of ultrasonic and ionizing irradiation on different organic compounds [1-6] we give in the present communication the results of studying the chemical transformations that take place in aqueous solutions of carbohydrates under the action of ultrasonic vibrations (USV). We studied starch and inulin, glucose and fructose, and also the disaccharides – maltose and sucrose. The existing literature data are completely insufficient for judging as to the nature of the products that are formed in the sonic exposure of carbohydrates [7-9].

Subjected to ultrasonic treatment were 0.25% solutions of polysaccharides and 0.14 M solutions of mono- and disaccharides. Chemically pure products were used in the study. All of the solutions were prepared with thrice distilled water. A description of the high-frequency generator used for obtaining the USV was given earlier [2]. The power output of the vibration contour generator was 300-400 W. The diameter of the piezo-quartz plate was 50 mm. The vibration frequency was 435 kHz. The sonic treatment of the solution, in an amount of 50 ml, was run in a stoppered conical flask. In this connection the temperature of the liquid was not permitted to rise above 42°. After a definite time interval samples were taken from the solution and were immediately analyzed in a SF-4 spectrophotometer. The measurements were made in the 230-300 mμ region in a cuvette with a layer thickness of 10 mm. Formaldehyde was determined in the spectrophotometer by the described method [10]. In determining the amount of COOH-group there was taken into consideration the amount of alkali that was required for the titration of the water itself, being subjected to ultrasonic exposure under these conditions.

For chromatographic analysis the chromatographic paper put out by the State Paper Mill No. 2 was used. The developer for the fructose and sucrose was 5 g of urea + 20 ml of 2 N HCl + 100 ml of ethyl alcohol. The mixture used as solvent was: butyl alcohol, acetic acid, water (5:4:1) [11]. For disclosing the glucose there were used the same solvent and a developer that consisted of 5 volumes of aniline dissolved in alcohol, 5 volumes of a 4% diphenylamine solution in alcohol (a fresh solution prepared each time) and 1 volume of concentrated phosphoric acid [12].

Action of ultrasonics on starch and inulin solutions. The results of the spectrophotometric measurements revealed that in starch solutions the action of ultrasound causes an increased absorption of ultraviolet light. However, the character of the absorption curves in starch solutions, depending on the duration of ultrasonic exposure, for example for 15 hours, hardly changed and the formation of maxima was not observed.

In inulin solutions the ultrasonic action also causes increased absorption. However, if the time of ultrasonic treatment is prolonged, for example more than 8 hours, there appears in the 256-300 mμ region a noticeable increase in the absorption of ultraviolet light with a maximum at 288 mμ (Fig. 1). Consequently, under the influence of ultrasonic exposure products are formed from the elementary starch and inulin units, differing in their ability to absorb ultraviolet rays.

By means of chromatography it was found that under the influence of ultrasonic exposure the inulin suffers hydrolytic decomposition with the cleavage of fructose. On the chromatogram for inulin solutions exposed to sonic treatments of 10 and 15 hours there distinctly appeared slightly colored spots, corresponding to the free fructose (R_f = 0.36). This permits the conclusion that under the influence of USV in the main valence chains of inulin there occurs rupture of the 1,2-bond between the fructose residues. In this connection the simultaneously progressing oxidation processes cause the formation of formaldehyde (Fig. 3) and the COOH-group [3] in the sonic treated inulin solutions.

Action of ultrasonics on glucose and fructose solutions. In connection with the data, obtained on the sonic treatment of starch and inulin, it appeared of interest to study the absorption of ultraviolet light by glucose and fructose solutions after ultrasonic exposure. Fig. 2 shows that in this connection the absorption increases in glucose solutions, although the absorption curves change their original character but slightly. Only under prolonged ultrasonic exposure, for 15 hours, does a maximum begin to appear at 270 mμ. Sharper changes take place in the fructose solutions under the influence of USV. After a 2-hour ultrasonic exposure there appears an absorption maximum in the fructose solutions at a wave length of 283 mμ. Further sonic treatment for 5, 10 and 15 hours causes a shifting of the maximum in the direction of increased absorption of the longer wave lengths.

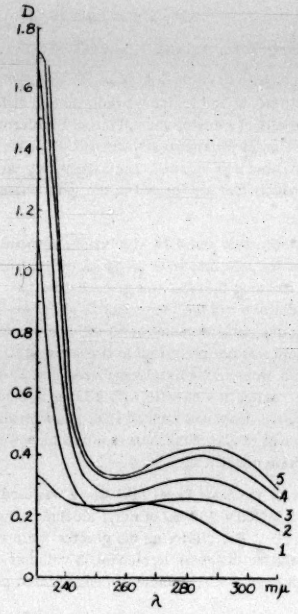

Fig. 1. Absorption curves for inulin solutions. Solutions: 1) not sonic treated; 2) sonic treated for 4 hours; 3) sonic treated for 8 hours; 4) sonic treated for 12 hours; 5) sonic treated for 15 hours.

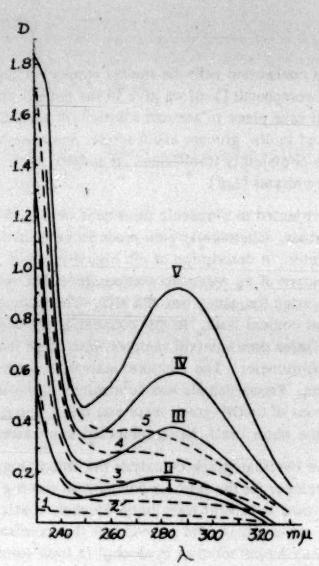

Fig. 2. Absorption curves for glucose and fructose solutions. Solutions: 1 and I) not sonic treated; 2 and II) sonic treated for 2 hours; 3 and III) sonic treated for 5 hours; 4 and IV) sonic treated for 10 hours; 5 and V) sonic treated for 15 hours. Arabic numbers – glucose; Roman numbers – fructose.

TABLE

Duration of sonic treatment (hours)	λ max (mμ)	
	fructose	inulin
2	283	–
4	–	282
5	285	–
8	–	283.5
10	286	–
12	–	287.5
15	287	288

It can be seen (Fig. 2) that under the influence of USV there occurs more intense decomposition of fructose than of glucose. This is also confirmed by the chemical study data [3]. From Fig. 3 it can be seen that for the same length of sonic treatment there is less formaldehyde formed in the glucose solutions than in the fructose solutions.

From a comparison of the results for the absorption of ultraviolet light in sonic-treated starch and glucose solutions, it can be concluded that among the products obtained in the oxidative decomposition of starch under ultrasonic exposure, other than aldehydes (Fig. 3) and organic acids [3], there fail to be present in appreciable amounts the substances that arise in the sonic treatment of free glucose. The curves for the absorption of ultraviolet light in fructose solutions, exposed to ultrasonic action, are similar to the absorption curves for the sonic treated inulin solutions. In both cases the ultrasonic action results in increased absorption and shifting of the maxima toward the longer wave lengths (see Table).

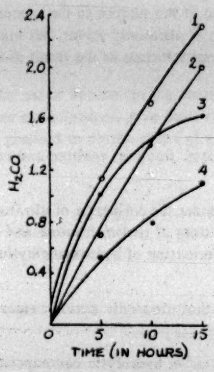

Fig. 3. Effect of ultrasonics on the formation of formaldehyde (in milligrams/100 milliliters) in solutions of fructose (1), glucose (2), inulin (3) and starch (4), as a function of the duration of sonic treatment.

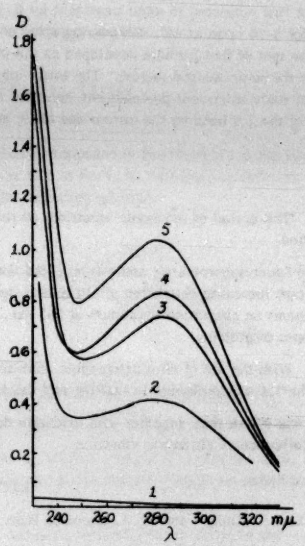

Fig. 4. Absorption curves for sucrose solutions. Solutions: 1) not sonic treated; 2) sonic treated for 5 hours; 3) sonic treated for 10 hours; 4) sonic treated for 12 hours; 5) sonic treated for 15 hours.

The data in the table show that from the inulin macromolecule under the influence of ultrasonics the same compounds are formed as also appear in the spectrum of sonic treated fructose. λ_{max} at 283 mμ in the fructose and inulin solutions corresponds to the absorption of hydroxymethylfurfural [13].

Action of ultrasonics on maltose and sucrose solutions. In connection with establishing the spectral changes in glucose and fructose solutions, proceeding in the field of ultrasonic waves, the effect of sonic treatment on maltose and sucrose was studied. The spectrophotometric data revealed that in maltose solutions under ultrasonic treatment there occurs increased ultraviolet light absorption, although in this connection the appearance of no maxima was observed. The destruction of maltose in the ultrasonics field was accompanied by the formation of formaldehyde, aldehyde groups and the COOH-group [3]. Chromatographic analysis permitted establishing the fact that in maltose under the action of USV for 10 and 15 hours there occurs rupture of the 1,4 oxygen bridge. On the chromatogram there appeared maltose spots (R_f = 0.14) and spots in their distribution corresponding to free glucose (R_f = 0.27).

In sucrose solutions (Fig. 4) the ultrasonic action causes increased ultraviolet light absorption and the appearance of maxima at 282.5-283 mμ. The latter indicate that in the sonic treatment of sucrose there occurs the formation of hydroxymethylfurfural from the fructose component. Under the influence of sonic exposure the sucrose suffers oxidative destruction; in this connection organic acids and formaldehyde are formed. For example, in sucrose solutions, exposed to ultrasonic action for 15 hours, in 100 ml there was formed 35.2 mg of COOH-group and 2.2 mg of formaldehyde. By chromatographic analysis it was established that the sucrose is hydrolyzed under ultrasonic action. Two spots could be seen on the chromatogram of the sonic treated sucrose. One corresponded to sucrose (R_f = 0.25); the other spot, less clear and higher situated as regards the travel rate coefficient, corresponded to fructose (R_f = 0.36). With increase in the time of sonic treatment the fructose spot became less intense; however, it was always weaker than the sucrose spot. We made an approximate evaluation of the amount of fructose, formed in the sonic treatment of sucrose, by the method of visually comparing the color of the spots on the chromatograms of the unknown and standard solutions [15]. After 5, 10 and 15 hours of ultrasonic action the amount of fructose was correspondingly 0.25, 0.5 and 1.25%.

To determine the effect of HNO_2 and HNO_3 on the hydrolysis of sugar, which acids are always formed in aqueous medium under the action of USV due to oxidative processes [14], sucrose solutions were prepared from water that had been first subjected to sonic treatment for 5, 10 and 15 hours, after which the solutions were placed in the thermostat for 5-15 hours at 42°. Chromatographic analysis revealed that partial hydrolysis of the sucrose takes place here: the spot of free fructose developed on the chromatogram. The chromatogram was similar to the chromatogram for the sonic-treated sucrose. The latter may indicate that decomposition of the sucrose to the monosaccharide under sonic treatment proceeds not under the influence of the direct action of ultrasonic waves, but via the hydrolysis of the 1,2 bond by the nitrous and nitric acids that are formed in aqueous solutions as the result of ultrasonic action.

SUMMARY

1. The action of ultrasonic vibrations on solutions of starch, inulin, glucose, fructose, maltose and sucrose was studied.

2. Spectrophotometric analysis revealed that in carbohydrate solutions under the influence of ultrasound there occurs increased absorption of ultraviolet light; in this connection in solutions of inulin, fructose and sucrose there appears an absorption maximum at 283 mμ, which may indicate the formation of hydroxymethylfurfural in the sonic treatment.

3. With the aid of chromatographic analysis on paper it was established that ultrasonic action causes a rupture of the 1,4 oxygen bridge in maltose and the 1,2 bond in sucrose.

It was shown that, together with oxidative destruction, the carbohydrates suffer hydrolytic decomposition under the influence of ultrasonic vibrations.

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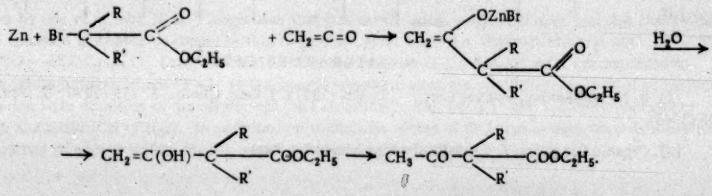
SYNTHESIS OF METHYL-β-KETO ACIDS

B. N. Dashkevich and Yu. Yu. Tsmur

The use of ketene (in the Seitz-Grignard reaction) as a carbonyl compound is described [1] in the literature. The latter circumstance gave basis to assume that the use of ketene also in the S. N. Reformatsky reaction [2] would make it possible to obtain esters of β-keto acids in accord with the following scheme:



Our experiments confirmed the fact that ketene behaves like a carbonyl compound in this reaction, and as a result esters of methyl-β-keto acids are obtained in fair yields (although we did not attempt to determine the optimum conditions for the given reaction).

On the basis of our molecular refraction determinations, in value being intermediate between the molecular refractions calculated for the keto and enol forms, it can be stated that, for example, the acetoacetic ester synthesized by us contains 54.54% of the enol form. The presence of appreciable amounts of the enol form was manifested in lowered boiling points for the synthesized esters and in the development of a reddish coloration with ferric chloride.

EXPERIMENTAL

The reaction between ketene and the esters of α-bromo acids was carried out in a special manner. In a 300 ml round-bottomed flask, fitted with condenser, dropping funnel and a tube reaching to the bottom for the addition of gaseous ketene, was placed the charge of activated zinc turnings and an iodine crystal. A mixture of the corresponding α-bromo ester and diethyl ether (1:2) was slowly added through the dropping funnel with the simultaneous passage of ketene in three times the amount calculated on the basis of its being obtained in 25% yield in the pyrolysis of acetone. The reaction was run for two hours. During the experiment the reaction flask was cooled with ice water. Ice water was used to decompose the formed complex with subsequent dissolution of the basic zinc salt by the addition of dilute sulfuric acid solution. The ether layer was dried over calcium chloride. We obtained the best results by letting the reaction mixture stand for a day and then heating on the water bath for one and a half hours. After distilling off the ether, the product was vacuum distilled and a definite fraction was collected, which was then analyzed. The experimental results are given in the Table.

SUMMARY

1. It was shown that in the S. N. Reformatsky reaction ketene (carbomethylene) behaves in exactly the same manner as in the Seitz-Grignard reaction, reacting like a carbonyl compound.

2. The preparation of methyl-β-keto acid esters by this method expands even more the utility of the S. N. Reformatsky reaction.

3. The method developed by us for the synthesis of methyl-β-keto acids can be used for preparative purposes.

4. It was established that the methyl-β-keto acid esters obtained by the described method contain more than 50% of the enol form.

TABLE

Expt. No.	Starting bromo ester		Obtained ester	Yield (%)	B.p. at pressure (mm)	Molecular weight		n_D^{20}	d_4^{20}	MR_D		
	Name	amount (g)				found	calc'd.			found	calc'd. enol form	calc'd. keto form
1	Monobromo-acetate	50	Acetoacetic*	32.9	69-72° (14)	126.14	130	1.4210 (18°)	1.0262 (18°)	32.158	32.620	31.573
2	α-Monobr-omopropion-ic	60	Methylaceto-acetic**	23.25	71-74 (13)	142.9	144	1.4295 (18°)	1.0160 (18°)	36.620	37.238	36.191
3	α-Monobr-omo-n-butyr-ic	40	Ethylaceto-acetic***	26.8	82-85 (12)	157	158	1.4310 (19°)	0.9790 (19°)	41.776	41.856	40.809

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* Semicarbazone, m.p. 127.5-128° (decomposition).

** 2,4-Dinitrophenylhydrazone, m.p. 163-164° (decomposition).

*** 2,4-Dinitrophenylhydrazone, m.p. 142-143° (decomposition).

REACTIONS OF ALIPHATIC DIAZO COMPOUNDS WITH UNSATURATED COMPOUNDS

XVIII. REACTION OF DIAZOACETIC ESTER WITH 1,3- AND 2,3-DIBROMOPROPENES AND α-ALLYL ACETATE

I. A. Dyakonov and T. V. Domareva

It was shown by one of us with N. B. Vinogradova that diazoacetic ester (ethyl) and allyl bromide react with each other in the presence of copper or copper sulfate to give the ethyl ester of α-bromoallylacetic acid (I) $CH_2=CH-CH_2-CHBr-COOC_2H_5$ [1]. Later the newly discovered reaction of diazoacetic ester was extended to other halides with labile halogen atoms [2-4]. In the present communication the possibility was studied of performing the same reaction with dihalides of the allyic type, and specifically with the 2,3- and 1,3-dibromopropenes $CH_2=CBr-CH_2Br$ and $CHBr=CH-CH_2Br$. In addition, we studied the action of diazoacetic ester on α-bromoallyl acetate in the presence of copper sulfate for the purpose of realizing the reaction:

$$CH_2=CBr-CH_2OCOCH_3 + N_2CH-COOC_2H_5 \xrightarrow{CuSO_4} CH_2-CBr-CH_2OCOCH_3 + N_2.$$
$$\quad\quad\quad

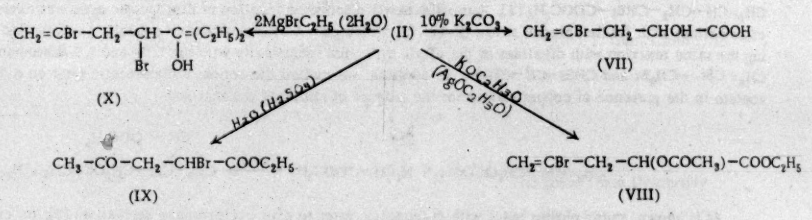
As is known, it is specifically with the aid of this reaction that the mutual position of the halogen atoms in halogenated compounds and in all other cases is determined [7].

Ester (III), the same as ester (II), is described here for the first time. Formula (III) was confirmed by analysis, molecular refraction and Raman spectrum. The positions of the double bond and bromine atom in ester (III) could be established on the basis of the obtained ozonolysis data:

$$(III) \xrightarrow[2H_2O]{O_3} HCOOH + HOOC-(CH_2)_2-COOH + HBr + C_2H_5OH.$$

Formic and succinic acids were obtained in a yield of about 58% of the theoretical. In addition, some formaldehyde was found (11.4% of the theoretical yield).

We also made other attempts to determine the structure of the ester (II); however, not one of them led to a positive result. In the alkaline hydrolysis of (II), instead of the expected hydroxy acid (VII) a polymer was isolated, and polymeric products were also obtained, when the conversion to the ester (VIII) was attempted.



Apparently, in both cases HBr was cleaved from the starting ester (II), and the resultant γ-bromovinylacrylic acid $CH_2=CBr-CH=CH-COOH$ or its ester then polymerized. It must be assumed that the cleavage of HBr is facilitated by the presence of a second bromine atom in the ester molecule, in the gamma-position with respect to the ester group, since in the action of alkaline agents on ester (I) the predominant reaction was the formation of the corresponding hydroxy acid [1]. Due to tar formation, we were also unable to obtain the individual substances when we used ester (II) in the organomagnesium synthesis (II → X) and in its hydration under the influence of sulfuric acid (II → IX). However, taking into consideration the results of the above given reactions on the dehalogenation of ester (II) and the ozonolysis of ester (III), it must be assumed that the structures of the esters have been established. This conclusion is supported by the analysis of the Raman spectra of esters (II) and (III) and the earlier described esters (I) and (IV), the spectra of which were taken for comparison. The presence of bromine in the alpha-position to the $-COOC_2H_5$ group in esters (I) and (II) causes a regular [8, 9] increase in the frequency of the C=O bond (1739 cm^{-1} for both esters) against a frequency of 1732 cm^{-1}, which characterizes the same bond in esters (III) and (IV), not having a bromine atom in the alpha-position. The presence of bromine in the gamma-position, i.e., "at the double bond", in esters (II) and (III) is characterized, on the other hand, by a regular [10] reduction in the frequency of the C=C bond (1630 cm^{-1} for both esters), when compared to esters (I) and (IV), not having bromine at the double bond [frequency of the C=C bond 1643 cm^{-1} for (I) and 1642 cm^{-1} for (IV)]. The C–Br bonds correspond to the following frequencies in the spectra of esters (I)–(III): 582 and 671 cm^{-1} for (I); 547, 620 and 683 cm^{-1} for (II) and 553 cm^{-1} for (III).

Apparently, 1,3-dibromopropene, in contrast to 2,3-dibromopropene, in general fails to react with diazoacetic ester in the manner found general for earlier studied alkyl [1-3] and aralkyl [4] halides. As the result of carrying out the corresponding experiment, with a 1:1* mole ratio of the reactants and $CuSO_4$ as catalyst, it was found that 55% of the dibromopropene (of the original weight) failed to react. In addition, the formation in the reaction of the decomposition product from diazoacetic ester, fumaric acid ester [5], was shown, and substances of a tarry nature were obtained. It must be assumed that the presence of halogen in the gamma-position facilitates the loss of 1,3-dibromopropene activity in this reaction. To give a theoretical explanation for this fact is, apparently, still difficult.

As was already indicated, the reaction with α-bromoallyl acetate was attempted here for the purpose of determining the possibility of obtaining the cyclopropane derivative. However, the results of the experiment proved

* Due to the difficult availability of 1,3-dibromopropene [11, 12] we avoided its use in excess in the reaction with diazoacetic ester.

to be quite unexpected: the addition of diazoacetic ester to α-bromoallyl acetate, warmed to 75° in the presence of copper sulfate as catalyst, caused polymerization of the entire reaction mass, in which connection at the end of the experiment we were unable to isolate any α-bromoallyl acetate, taken in double the calculated amount, from the reaction mass. Apparently, the polymerization of the bromoallyl acetate was due to the biradicals $>CH-COOC_2H_5$, formed in the decomposition of the diazoacetic ester, and it must be assumed that the presence of bromine at the double bond in the first of these compounds increases the polymerization tendency when compared with the earlier-studied unsubstituted allyl acetate.

The authors express their gratitude to Ya. E. Shmulyakovsky for taking the Raman spectra of the four ester (I-IV) samples.

EXPERIMENTAL

I. Condensation of Diazoacetic Ester with 2,3-Dibromopropene. Ethyl ester of α,γ-dibromoallylacetic acid (II). A mixture of 371 g of 2,3-dibromopropene [13] and 1.5 g of copper sulfate was heated with stirring to 100° (mixture temperature) and from a dropping funnel was added a solution of 151.4 g of diazoacetic ester* in 300 g of 2,3-dibromopropene. The evolution of nitrogen began only when the temperature was raised to 130°. Then the temperature of the mixture was maintained at about 120°, and the diazoacetic ester solution was added at such a rate that the evolution of nitrogen was not too rapid. At the end of the experiment the amount of evolved nitrogen was 27.6 liters (0°, 760 mm), i.e., 92.6% of the theoretical amount. The reaction mixture was filtered from the catalyst, and the excess dibromopropene was vacuum distilled at 50 mm. The recovery was 428.5 g. From this the amount of reacted dibromopropene was 243.5 g, or 96.5%, calculated on the original diazoacetic ester. The remainder of the reaction product was vacuum distilled from a tarry residue and then fractionated through a vacuum column: 1st fraction (intermediate) b.p. 35° at 6 mm, 94° at 3 mm – 26.5 g; 2nd fraction [ester (II)] b.p. 94-96° at 3 mm, 110-112° at 11 mm – 190.2 g (54.9%).

Ester (II) was analyzed and its constants determined.

d_4^{20} 1.665, n_D^{20} 1.503, MR_D 50.79; calculated 51.24.

Found %: Br 55.59, 55.94. M 293.5, 282.6. $C_7H_{10}O_2Br_2$. Calculated %: Br 55.89. M 286.0.

Ethyl ester of γ-bromoallylacetic acid (III). To a mixture heated to 60° of 35 g of ester (I), 30 ml of alcohol and 10 ml of 50% acetic acid was added with stirring and in small portions 30 g of zinc dust. After heating for 1 hour on the water bath the unreacted zinc was filtered, and to the filtrate was added dry soda to weakly acid (to litmus) reaction. Then the solution was extracted with ethyl ether, and the ether extracts were finally neutralized by shaking with a 10% soda solution, and dried over sodium sulfate. After distilling off the solvent the residue was vacuum distilled. B.p. 89.5-90.5° at 15 mm, 80.5-81.5° at 10 mm. Yield 22.5 g (89.2%).

d_4^{20} 1.315, n_D^{20} 1.465, MR_D 43.31; calculated 43.51.

Found %: Br 38.90, 39.13. $C_7H_{11}O_2Br$. Calculated %: Br 38.64.

Ozonolysis of ester (III). Ozone (4%) was passed into a solution of 6 g of ester (III) in 50 ml of chloroform, cooled externally with an ice-salt mixture. After the completion of ozone absorption (4 hours and 20 minutes, 1.808 g O_3) and removal of the chloroform the ozonide was decomposed by heating with water. The obtained water solution was made up to 500 ml, and from it were taken two 50 ml aliquots for the quantitative determination of formaldehyde and formic acid. The first sample was boiled for 2 hours with a 4% dimedon (0.8 g) solution. The weight of the dimedon derivative was 0.097 g, which, calculated as formaldehyde, is 11.9%. M.p. 187-188° (from alcohol). Literature m.p. 189° [15].

To the second sample was added 2 g of potassium acetate (to bind the hydrobromic acid) and the amount of formic acid was determined by means of the Kucherov reagent (0.1 g of $HgCl_2$ in 1 ml of water). The obtained Hg_2Cl_2 precipitate weighed 0.7895 g which, calculated as formic acid, is 57.9% of the theoretical amount (if it is assumed that the terminal methlene groups in ester (III) are completely converted into this acid). The total yield of CH_2O and HCOOH was 69.8%.

The remaining water solution of the ozonolysis products (400 ml) was concentrated on the water bath. The succinic acid obtained in this manner weighed 1.6 g (58.8%). M.p. 180-181°. After recrystallization from water, m.p. 183°. Weight 1.4 g (51%).

Found by titration: equiv. 59.2, 58.7. $C_2H_4(COOH)_2$. Calculated: equiv. 59.0.

* Purified by steam distillation in vacuo [14].

Alkaline hydrolysis of ester (II). The ester (II) (28.6 g) was hydrolyzed by heating with a 10% potassium hydroxide solution (275 ml). The obtained dark red solution was made neutral by the addition of 10% sulfuric acid, and the alcohol formed in the hydrolysis was steam distilled. The solution remaining in the distillation flask was made acid to Congo with sulfuric acid. The resultant brownish tarry product (4.5 g) is quite rapidly transformed into a hard polymer, insoluble in alcohol, chloroform, petroleum ether and in other organic solvents. The same product was isolated in the ether extraction of the residual acid water solution.

Action of potassium and silver acetates on ester (II). 1) Potassium acetate. A mixture of 7.1 g of ester (II), 2.5 g of anhydrous $KC_2H_3O_2$ and 30 ml of anhydrous alcohol was heated for several hours on the water bath under reflux. The filtered precipitate was treated with water to dissolve potassium bromide. The water-insoluble portion (1 g) was a colorless rubbery polymer. The alcohol filtrate was diluted with water (100 ml), and the resultant oil after drying was vacuum distilled. It was not possible to investigate the distillate with b.p. 95-109° at 6 mm and n_D^{16} 1.498-1.491, due to the small amount (1.2 ml) obtained. The residue in the distilling flask was a hard, almost colorless polymer (3.5 g).

2) Silver acetate. A mixture of 5.2 g of ester (II), 3.9 g of silver acetate and 30 ml of anhydrous alcohol was heated with vigorous stirring on the water bath for 2 hours. The filtered solution was diluted with water and the separated oil was extracted with ether. Distillation of this oil in vacuo gave 4.2 g of unchanged ester (II) with b.p. 104-105° at 8 mm and n_D^{16} 1.503.

Action of 80 and 95% sulfuric acid on ester (II) (hydration). 1) 80% sulfuric acid. A mixture of 7.1 g of ester (II) and 34.6 g of 80% sulfuric acid was heated with mechanical stirring for 3 hours at 50°. We failed to observe either solution of the ester layer or HBr evolution. The mixture was poured on ice, the sulfuric acid was neutralized with soda, and the oil was extracted with ether and vacuum distilled; there was obtained 3 g of unchanged ester (II) with b.p. 84-86° at 2 mm and n_D^{16} 1.504. Testing of the water solution, separated from the oil, with p-nitrophenylhydrazine revealed the absence of any carbonyl-containing compounds in the solution.

2) 95% sulfuric acid. A mixture of 14.3 g of ester (II) and 30 ml of concentrated sulfuric acid was stirred in the cold for 2 hours: solution of the ester and the evolution of HBr was observed. The dark red solution was then treated as indicated above. The obtained oil was vacuum distilled: b.p. 94-127° at 6 mm (with decomposition toward the end of distillation). The distillate gave a qualitative test for the C=O group (semicarbazone with m.p. 181-182°, from alcohol), but we were unable to isolate the carbonyl-containing ester (IX) from the mixture.

Attempted preparation of the bromo alcohol (X) and its corresponding oxide. For 1 mole of the ester there were used 2 moles of ethylmagnesium bromide under Grignard reaction conditions. The organomagnesium complex from the reaction was decomposed with dilute acetic acid. A dark oil was isolated from the ether extracts, which when vacuum distilled at 10 mm decomposed with the formation of tarry products. An attempt was made to obtain the α-oxide from the hypothetical alcohol (X), not isolating it from the ether solution after running the Grignard synthesis. For this purpose the dried ether solution was treated with finely pulverized potassium hydroxide. However, we were unable to isolate the α-oxide: vacuum distillation of the reaction product resulted in decomposition with the formation of tar.

II. Condensation of Diazoacetic Ester With 1,3-Dibromopropene. The 1,3-dibromopropene was prepared by us in accord with the method of Braun and Kuhn [12] by the action of phosphorus oxybromide on glycerol α,γ-dibromohydrin. According to the data of the German chemists, the yield of the dibromopropene is 35-40% of the theoretical. However, using this method we were able to obtain only 6% of the theoretical yield. It should be mentioned that the yield according to the method of Lespieau [11] (action of P_2O_5 on glycerol α,γ-dibromohydrin), apparently, also fails to exceed 10% of the theoretical [12]. The foreign chemists, as well as the present authors, failed to separate the cis- and trans- isomers of 1,3-dibromopropene, operating with their mixture.* Recently [16] 1,3-dibromopropene was obtained by a new method, and both isomers were isolated in pure form: cis-isomer, b.p. 60° at 25 mm, d_4^{20} 2.0599, n_D^{20} 1.5550; trans- isomer, b.p. 66° at 25 mm, d_4^{20} 1.9791, n_D^{20} 1.5495. Our 1,3-dibromopropene had b.p. 150-156° and d_4^{20} 2.049.

Condensation. To a mixture heated to 60° of 30 g of 1,3-dibromopropene and 0.07 g of $CuSO_4$ (anhydrous) with mechanical stirring was slowly added 16.3 g of diazoacetic ester. At the end of the experiment the amount of evolved nitrogen was 3 liters (16°, 769.5 mm) i.e., 90.7% of the possible theoretical. The cooled reaction product was filtered from the catalyst, and the filtrate was vacuum distilled: 1st fraction b.p. 45-60° at 13 mm, 16.5 g; 2nd fraction b.p. 60-100° at 13 mm, 2.3 g. The not distilled tarry residue weighed 12 g. Repeated distillation of the first fraction gave 12 g of the original dibromopropene with b.p. 151-157°. However, both its density

* Apparently, as the result of this the physical constants, given in the literature, differ markedly.

and refractive index proved to be lowered: d_4^0 1.979, d_4^{20} 1.943, n_D^{20} 1.538, which could be explained as being due to the presence of diethyl fumarate (b.p. 98-99° at 14 mm, d_{20}^{20} 1.054, n_D^{20} 1.4410 [17]), as impurity. The presence of the latter was actually demonstrated in the fraction with b.p. 60-100° at 13 mm. From this fraction 2.3 g of substance was hydrolyzed by heating with 20 ml of a 10% alcohol solution of sodium hydroxide. The resultant disodium salt of fumaric acid after drying weighed 2.1 g. One gram of the salt was dissolved in 10 ml of water, and the obtained solution was boiled with 15 ml of an alcohol solution of phenacyl bromide (2.5 g). The diphenacylfumarate weighed 0.8 g and after recrystallization from alcohol failed to show a depression of the melting point (195-196°) when mixed with the authentic specimen.

III. Condensation of Diazoacetic Ester with α-Bromoallyl Acetate. To a mixture heated on the water bath of 73 g of α-bromoallyl acetate $CH_2=CBr-CH_2OCOCH_3$ [11] and 0.5 g $CuSO_4$ with mechanical stirring was added a solution of 46.8 g of diazoacetic ester in 74 g of α-bromoallyl acetate. The evolution of nitrogen began at 74° (bath temperature). At the end of the experiment the amount of evolved nitrogen was 9.3 liters (15°, 770.1 mm), or 95.8% of the calculated. Already during the reaction a thickening of the liquid in the reaction flask was noted. When all of the diazoacetic ester had been added the reaction product was a viscous, yellow polymeric mass, not distillable in vacuo without decomposition. The distillate contained substances boiling below the original bromoallyl acetate (evidently, due to thermal decomposition of the polymer), and the excess α-bromoallyl acetate (1 mole) taken for reaction could not be isolated by distillation. For this reason it must be assumed that in this reaction the α-bromoallyl acetate is completely polymerized.

Raman Spectra of Esters I-IV

An ISP-51 three-prism spectrograph was used for taking the spectra. Slit width 0.04 mm; exposure time 6 hours. Glass light filter. Hg 436. A 20-division scale was used in the photometric measurement of the spectral line intensities.

Ester (I), $\Delta\nu$: 182 (3), 247 (1), 283 (6), 308 (1), 330 (0.5), 371 (2w), 413 (1), 582 (2), 671 (3), 798 (10), 858 (9), 903 (0.5), 931 (3), 964 (2), 997 (1), 1023 (2), 1066 (1), 1103 (3), 1115 (4), 1152 (2), 1176 (1), 1234 (2), 1261 (2), 1303 (10w), 1418 (8), 1452 (6), 1643 (20), 1739 (6), 2872 (2), 2930 (15), 2980 (20), 3014 (8), 3084 (8).

Ester (II), $\Delta\nu$: 167 (1), 206 (4), 276 (1), 365 (7), 421 (1), 547 (6), 580 (2), 620 (2), 683 (3), 801 (9), 853 (10), 924 (3), 961 (1), 986 (1), 1017 (1), 1099 (2), 1116 (3), 1153 (1), 1185 (1), 1233 (2), 1255 (3w), 1305 (1), 1343 (1), 1405 (6w), 1450 (6), 1630 (20), 1739 (6), 2873 (4), 2934 (15), 2985 (20), 3038 (2), 3105 (8).

Ester (III), $\Delta\nu$: 166 (1), 331 (2), 360 (10w), 527 (4), 553 (8), 797 (2), 855 (10), 889 (2), 935 (3), 1016 (3), 1058 (3), 1111 (4w), 1153 (2), 1173 (1), 1234 (2), 1263 (2), 1300 (3w), 1401 (6), 1422 (4), 1450 (6), 1631 (20), 1732 (6), 2872 (2), 2929 (15), 2980 (10), 3097 (8).

Ester (IV), $\Delta\nu$: 192 (1), 295 (2), 366 (4), 419 (1), 791 (1), 856 (8), 917 (2), 937 (2), 990 (2), 1053 (2), 1097 (2), 1112 (4), 1161 (1), 1200 (1), 1238 (1), 1295 (10), 1417 (8), 1449 (6), 1642 (20), 1732 (6), 2872 (3), 2922 (20), 2980 (10), 3005 (8), 3050 (8).

SUMMARY

1. The reaction of diazoacetic ester (ethyl) with 2,3-dibromopropene in the presence of copper sulfate leads to the formation of the ethyl ester of α,γ-dibromoallylacetic acid (II) in a 50-55% yield of the theoretical. The investigated reaction proceeds in a manner similar to the reaction of diazoacetic ester with allyl bromide.

2. The action of zinc dust and acetic acid on ester (II) gives the ethyl ester of γ-bromoallylacetic acid (III). Its structure was established by ozonolysis. Both esters are new.

3. The Raman spectra of esters (II) and (III) were taken, and also of the earlier obtained esters of α-bromoallyl (I) and allylacetic acid (IV). The spectral data can be used for confirming the structures of esters (I-IV).

4. The alkaline hydrolysis of ester (II), and also the action on it of potassium acetate in alcohol solution, leads to the formation of polymeric substances. Ester (II) fails to be hydrated under the influence of sulfuric acid and fails to be converted into the tertiary alcohol under the conditions of the Grignard reaction.

5. 1,3-Dibromopropene fails to react with diazoacetic ester in the manner indicated for the 2,3-dibromopropene, while α-bromoallyl acetate under the conditions of this reaction is polymerized.

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•••••• See Consultants Bureau Translation, page 1399.

CHLORINATION OF SATURATED NITRILES

F. N. Stepanov and N. I. Shirokova

While the saturated carboxylic acids and many of their derivatives belong to the class of compounds that are readily chlorinated in the α-position, the saturated nitriles chlorinate with great difficulty.

As early as 1876 Backunts found [1] that acetonitrile chlorinates very slowly in the presence of iodine either in the cold or on heating. Only after the passage of chlorine for 5 days was it possible to achieve almost complete chlorination, in which connection all three hydrogens of the methyl group were replaced by chlorine. In another paper [2] by the same author we find that propionitrile also chlorinates with difficulty with the formation of the α,α-dichloro derivative. According to a German patent issued in 1942 [3] acetonitrile is chlorinated under intense illumination at 50-70°. Mention is made of the extremely slow chlorination rate, which also leads to the formation of the trichloro derivative. According to an American patent issued in 1947 [4] acetonitrile is chlorinated in the vapor phase at 320-440° over metallic catalysts. Here also the trichloroacetonitrile is obtained.

An examination of the literature data on chlorination in the liquid phase* indicates contradiction in that the extremely slow reaction rate always leads to exhaustively chlorinated products. To find the mono- and dichloro-derivative (the latter in the case of acetonitrile) in the reaction mixture is impossible.

This contradiction is most easily explained if it is assumed that the chlorination rate of the original nitrile is considerably slower than the chlorination rate of the partially chlorinated products. However, such an assumption possesses very little probability, since it has no analogy. The stepwise chlorination of the carboxylic acids themselves and of their derivatives is very easily accomplished. The same is also true of many other compounds, possessing sufficiently active methyl and methylene groups.

More probable is the assumption that the hydrogen chloride liberated in the chlorination process adds to the partially chlorinated nitrile, and the formed nitrile salt or its tautomeric imide chloride is chlorinated at a much faster rate than the original nitrile:

$$CH_3-CN + Cl_2 \xrightarrow{slow} (CH_2Cl-C{\equiv}NH)^+ Cl^-,$$

$$(CH_2Cl-C{\equiv}NH)^+ Cl^- + Cl_2 \xrightarrow{fast} (CHCl_2-C{\equiv}NH)^+ Cl^- + HCl,$$

$$(CHCl_2-C{\equiv}NH)^+ Cl^- + Cl_2 \xrightarrow{fast} (CCl_3-C{\equiv}NH)^+ Cl^- + HCl,$$

$$(CCl_3-C{\equiv}NH)^+ Cl^- \xrightarrow{heating} CCl_3-CN + HCl.$$

From this assumption it directly follows that preliminary treatment of the nitrile with hydrogen chloride should greatly accelerate its chlorination rate. This conclusion was fully confirmed experimentally.

As is known, acetonitrile absorbs dry hydrogen chloride below 40°, while at higher temperatures the addition product dissociates. If to dry acetonitrile there is added, at a temperature not exceeding 40°, approximately 0.1-0.2 mole of hydrogen chloride and then chlorine is passed, the latter immediately begins to react, proceeding with great rapidity and with the evolution of heat, in the dark and without any catalysts [5]. Then for continuous reaction it is necessary to maintain the temperature at 36-42°, regulating it by the rate of chlorine addition and external cooling. If the temperature is allowed to rise above the indicated range there is rapid cleavage of the bound hydrogen chloride and the rate of chlorine absorption drops, reaching an extremely low value when all of the hydrogen chloride has been removed. On the other hand, at slightly too low a temperature the formed hydrogen chloride combines with the reaction mass, which leads to difficulties in subsequent treatment. In addition, the chlorination rate drops at low temperatures. It is expedient to only partially chlorinate the acetonitrile, up to the formation of the azeotropic mixture: acetonitrile-trichloroacetonitrile, containing 79% of the latter. More profound chlorina-

* Vapor phase chlorination is not specific, since saturated hydrocarbons also chlorinate under these conditions.

tion leads to the formation of a slightly larger amount of tarry products.

The chlorination of propionitrile under these conditions is even smoother. Dichloropropionitrile fails to form an azeotropic mixture with propionitrile; hardly any tarry impurities are formed in this case, and here it is expedient to carry the chlorination to completion, and to isolate the finished product by the direct distillation of the chlorinated liquid.

It is possible to explain the catalytic influence of hydrogen chloride in the following manner. The hydrogen chloride adds reversibly to the nitrile with the formation of the nitrile salt, tautomeric with the imide chloride:

$$CH_3-CN + HCl \longrightarrow (CH_3-C{\equiv}NH)^+ Cl^- \rightleftharpoons CH_3-\underset{Cl}{C}=NH.$$

The added hydrogen chloride communicates an elementary positive charge to the nitrile group, localized for the most part at the carbon atom. In this way is explained, on the one hand, the tautomerism: nitrile salt-imide chloride, and on the other hand, the ability of nitrile salts (imide chlorides) to add anions of the type $(OR)^-$ and $(H_2)^-$ with the formation of imino ethers and amidines. The positive charge on the carbon atom of the nitrile group polarizes the adjacent carbon atom of the methyl (methylene) group, which explains the greater chlorination rate, proceeding here, apparently, by the ionic mechanism.

According to N. D. Zelinsky, a similar phenomenon occurs in the halogenation of carboxylic acids: the acid halides are more easily halogenated than the acids.

EXPERIMENTAL

Trichloroacetonitrile. Into 500 g of dry acetonitrile was introduced 50-60 g of hydrogen chloride, maintaining the temperature (external cooling) not to exceed 36°. Without lowering this temperature, chlorine was passed at a rate of 500-600 ml a minute. During the chlorination, lasting 10-12 hours, the temperature was regulated in the limits 35-42°. The chlorination was terminated when the reaction liquid reached d 1.17. The azeotropic mixture boiling at 74-76° was distilled through a short column and then a small amount of unreacted acetonitrile was collected. The azeotropic mixture, weighing 690-700 g, was washed (6 times with 200 ml portions) with ice water to remove the acetonitrile. The washed product was dried over calcium chloride and distilled, collecting the fraction boiling at 84-86°. The yield of trichloroacetonitrile was 550 g.

The substance was identified as the tri-(trichloromethyl)-1,2,3-triazine [6], m.p. 94-95° (m.p. 93-95° [6]).

Dichloropropionitrile. Thirty grams of dry propionitrile was saturated with 30-40 g of hydrogen chloride at 35-40° (external cooling). The rate of chlorine addition was 500-600 ml a minute at the same temperature. The chlorination was terminated after the absorption of 240 g of chlorine, which required 4-5 hours. The chlorinated liquid was distilled through a short column. After distilling off the excess propionitrile the dichloropropionitrile was collected at 103-105°. Yield 235 g (90%, based on reacted propionitrile).

SUMMARY

1. The chlorination rate of saturated nitriles is increased considerably if the nitrile to be chlorinated is first treated with 0.1-0.2 mole of hydrogen chloride.

2. The increased reaction rate can be explained as being due to the structural characteristics (polar nature) of the product obtained in the addition of hydrogen chloride to the nitrile.

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REACTION OF VINYL ETHERS WITH AMINES

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The reaction of amines with vinyl acetate [1] and the vinyl esters of some otheracids [2] was described by us earlier. In the reaction of vinyl acetate with phenylhydrazine it was observed that not only the acetyl, but also the vinyl radical, reacted [1]. In connection with this we undertook a study of the reaction of amines with straight vinyl ethers.

From the literature it is only known that methyl vinyl ether reacts with ammonia at 200° and 200 atm, giving 2-methyl-5-ethylpyridine [3]. It is indicated that in the action of acetylene on N-phenylethanolamine the first product to be formed is the corresponding vinyl ether, which then cyclizes to N-phenyloxazoline [4]. It is quite possible that an analogous self-condensation process also took place in the experiments of M. F. Shostakovsky, I. A. Chekulaeva and N. A. Gershtein [5], who observed the formation of secondary products in the vinylation of ethanolamine.

In 1951-1952 it was shown by us that diethylamine and piperidine under prolonged heating with butyl vinyl ether in an ampoule at 100-110° were recovered unchanged. Also aniline and N-ethylaniline failed to react. In the presence of small amounts of the corresponding amine hydrochloride the heating of diethylamine with butyl vinyl ether gave a tarry mass, while aniline under the same conditions gave quinaldine in excellent yield. In an analogous manner the 2,6- and 2,8-dimethylquinolines [6] were respectively, obtained from the p- and o-toluidines.

A more detailed study of this reaction revealed that it also proceeds under the influence of benzoyl peroxide or the etherate of boron fluoride, but the yields in these cases are lower. Zinc chloride fails to catalyze the reaction. The best yields were obtained when 0.2-2 g of the hydrochloride was used for 1 mole of amine. The reaction fails to proceed with the pure hydrochloride (without free amine) in dioxan medium. If an excess of butyl vinyl ether is taken, then the yield of quinaldine (or correspondingly, 2,6-dimethylquinoline) fails to exceed 20-30%; on introducing an excess of the amine the yield is raised considerably. This observation agrees with the data of B. A. Ardashev [7], who came to the conclusion that an excess of the amine is needed in the synthesis of quinaldines. By using a solvent it is possible to reduce the amount of excess amine; however the optimum yields were obtained with an amine:vinyl ether ratio of 2:1. Replacement of the butyl vinyl ether by the isobutyl vinyl ether fails to signif-icantly affect the yield. With ethyl vinyl ether the yield is somewhat lower. At times in the synthesis of quinaldines, according to Doebner-Miller, the introduction of oxidizing agents [8, 9] is recommended for improving the yield. In our experiments the additions of the corresponding nitro compounds failed to exert an appreciable influence on the yields of quinaldines. It should be mentioned that in carrying out this reaction (as is customary in the preparation of quinaldines) the chief difficulty encountered is the isolation of the pure compound from the reaction mixture. The reaction slowly proceeds by itself even at room temperature (20-30 days); at 100° about 5 hours is required, while at 130° it is completed in 1-2 hours (although with considerable tar formation). The reaction is best carried out in sealed ampoules (or in a solvent), since tar formation is always observed when the reaction mixture is heated in a flask under reflux.

To check on the generality of the method we reacted butyl vinyl ether with p-anisidine, β-naphthylamine and o-aminophenol and obtained the corresponding quinaldines. It was revealed that aniline with pyrotartaric acid and butyl vinyl ether reacts vigorously, giving 2-methylcinchoninic acid. As a result, also in the synthesis of cinchoninic acids it is possible to replace the acetaldehyde by straight vinyl ethers.

At the time that the present study was being prepared for publication there appeared a paper [10], in which the synthesis of quinaldines, proceeding from butyl vinyl ether, was described. The authors of this paper conduct the reaction under somewhat different conditions (in an excess of hydrochloric acid). With the exception of aniline and p-toluidine, we took different starting amines. It is difficult to compare yields, since the authors of the paper used a different separation method (acylation with phthalic anhydride) and failed to indicate the yield in the case of p-toluidine.

EXPERIMENTAL

Quinaldine. A. To a mixture of 9.3 g of aniline and 0.2 g of aniline hydrochloride, heated to 95-100°, with stirring was added dropwise 5 g of butyl vinyl ether at such a rate that the reaction mixture remained at a gentle boil (2 hours); then stirring was continued for another 4 hours, gradually raising the bath temperature to 130°. The butyl alcohol (3.7 g, i.e., the calculated theoretical amount) was distilled from the reaction mixture, while the residue was vacuum distilled. The aniline with b.p. 55-63° (4 mm) distilled first, and then 2.7 g of quinaldine (80%) with b.p. 84-90° (4 mm), picrate, m.p. 190-191°. The preparation even after repeated vacuum distillations through a Widmer column contained aniline as impurity (when treated with benzenesulfochloride the benzenesulfanilide with m.p. 102-105° was isolated). The same yield was obtained when the mixture was allowed to stand for 25 days at room temperature (in a sealed ampoule). In a similar manner on using 0.01 g of benzoyl peroxide instead of the aniline hydrochloride the crude quinaldine was obtained in a 34% yield. On adding 5 ml (0.8 mole) of an ether solution of boron fluoride as catalyst the yield was 36%.

B. A mixture of 18.6 g (0.2 mole) of aniline, 10 g (0.1 mole) of butyl vinyl ether, 0.5 g of aniline hydrochloride and 40 ml of xylene was heated in a flask with reflux condenser on the boiling water bath for 25 hours, acidified with 50% sulfuric acid, the xylene and butyl alcohol removed by steam distillation, the residue made alkaline, the free bases removed by steam distillation and then separated by means of benzenesulfochloride. The yield of quinaldine with b.p. 108° (6 mm) was 3.4 g (48%), picrate, m.p. 191°. In an analogous experiment when acetic anhydride was used for the separation the yield of quinaldine was 4.0 g (57%), b.p. 109° (7 mm). When zinc chloride was used for the separation the yield was 33%. Substitution of dioxan for the xylene failed to raise the yield. Without solvent the yield dropped to 33%.

From aniline and ethyl vinyl ether the yield of quinaldine was 30%; from aniline and isobutyl vinyl ether it was 34%.

2,6-Dimethylquinoline. A mixture of 21.4 g (0.2 mole) of p-toluidine, 10 g (0.1 mole) of butyl vinyl ether and 0.5 g of p-toluidine hydrochloride was heated in a sealed ampoule for 20 hours at 100°. After cooling, the ampoule was opened, the butyl alcohol distilled off, the residue made strongly alkaline, and the free bases removed by steam distillation. The distillate was extracted with ether, the ether extract dried over fused caustic, the ether distilled off, and the residue vacuum distilled. The p-toluidine (15 g) with b.p. 70-80° (6 mm) distilled first, and then 5.8 g (74%) of crude 2,6-dimethylquinoline with b.p. 115-123° (7 mm). For purification the 2,6-dimethylquinoline was treated with benzenesulfochloride. The yield of 2,6-dimethylquinoline was 3.9 g (51%), b.p. 106-107° (4 mm), m.p. 59.5° (from ether). The melting point was not depressed when mixed with authentic 2,6-dimethylquinoline (m.p. 58-59°). Picrate, m.p. 186° (from alcohol).

Literature data: b.p. 125-133° (12 mm), m.p. 60° [8], picrate m.p. 186-187° [11].

In an analogous experiment, but using acetic anhydride for the separation, the yield was 54%, with additions of nitrobenzene or p-nitrotoluene the yield was 48-50%. If the calculated amount of amine is taken, then the yield is 26%; the addition of dioxan in this case raises the yield to 45%. In an analogous manner from p-toluidine and ethyl vinyl ether (separation by means of benzenesulfochloride) the yield of 2,6-dimethylquinoline was 36%, b.p. 95-99° (2 mm), m.p. 57°.

2,8-Dimethylquinoline. A mixture of 21.4 g (0.2 mole) of o-toluidine, 10 g (0.1 mole) of butyl vinyl ether, 0.5 g of o-toluidine hydrochloride and 50 ml of dioxan was heated in a flask under reflux for 25 hours. After distilling off the dioxan and butyl alcohol, followed by subsequent vacuum distillation, there was obtained 5.2 g (66%) of 2,8-dimethylquinoline with b.p. 108-112° (7 mm). In an analogous experiment, beznenesulfochloride was used for the separation of the free bases; the yield of pure 2,8-dimethylquinoline was 44% of the theoretical. When acetic anhydride was used for the separation the yield was 58%, b.p. 103-104° (5 mm); picrate, m.p. 180-181°. The mixed melting point with the picrate of authentic 2,8-dimethylquinoline failed to show a depression. When the reaction was run for 10 hours the yield was reduced to 30-35%.

Literature data: b.p. 252° [8], picrate, m.p. 180° [12].

2-Methyl-6-methoxyquinoline. To a mixture of 12.3 g (0.1 mole) of p-anisidine, 0.5 g of p-anisidine hydrochloride and 50 ml of dioxan, heated to the boil, with stirring was added dropwise 10 g (0.1 mole) of butyl vinyl ether over a period of 2 hours. Then the mixture was heated under reflux for another 16-18 hours, the butyl alcohol and dioxan distilled off, and the residue vacuum distilled twice. The yield of 2-methyl-6-methoxyquinoline was 1.2 g (15%), b.p. 120-123° (3 mm), m.p. 65°. After recrystallization from ether, m.p. 67°.

Literature data: b.p. 169-170° (18 mm); m.p. 67-68.5° [13].

In an analogous experiment, carried out at a lower temperature (30 hours, 80°) in an ampoule, the yield was 7%. When heated without dioxan in an ampoule for 4 hours at 105-110° the p-anisidine remained unchanged.

2-Methyl-5,6-benzoquinoline. A mixture of 14.3 g (0.1 mole) of β-naphthylamine, 10 g (0.1 mole) of butyl vinyl ether, 0.5 g of β-naphthylamine hydrochloride and 50 ml of dioxan was heated in a sealed ampoule for 25 hours at 100°. On conclusion of reaction the cooled ampoule was opened, the dioxan and butyl alcohol distilled off (to 125°), and the residue treated with 20 ml of acetic anhydride and boiled for 2 hours in a flask under reflux. Then, having diluted with water (100 ml), hydrochloric acid was added, the acetonaphthalide extracted with ether (2-3 times), the residue made strongly alkaline and the free bases distilled with steam, superheated to 180-190°. The distillate was extracted with ether, dried over fused caustic and after removal of the ether there was obtained 2.7 g (29%) of 2-methyl-5,6-benzoquinoline with m.p. 81-82° (from ether), picrate, m.p. 221° (from alcohol).

Literature data: m.p. 82°, picrate m.p. 220-221° [14].

If the calculated amount of β-naphthylamine is taken (in dioxan; 8 hours, 100-120°) the yield is 7%.

8-Hydroxyquinaldine.* A mixture of 10.9 g (0.1 mole) of o-aminophenol, 20 g (0.2 mole) of butyl vinyl ether, 50 ml of dioxan and 0.5 g of aniline hydrochloride was heated in a flask under reflux for 20 hours. Then the butyl alcohol and dioxan were removed by vacuum distillation, the residue was treated with a saturated soda solution, and the free bases were steam distilled. The distillate was acidified with concentrated hydrochloric acid, evaporated, neutralized with soda, and the obtained crystals separated. There was extracted 0.75 g (10%) of 8-hydroxyquinaldine with m.p. 70° (from alcohol). After distillation, m.p. 74°.

Literature data: m.p. 74° [15].

A 2% alcohol solution of 8-hydroxyquinaldine gives yellow precipitates in neutral medium with aqueous solutions of La^{+++} and Pr^{+++} salts.

2-Methylcinchoninic acid. A mixture of 9.3 g (0.1 mole) of aniline, 10 g (0.1 mole) of butyl vinyl ether, 8.8 g (0.1 mole) of pyrotartaric acid, 40 ml of anhydrous ethyl alcohol and 0.5 g of aniline hydrochloride was prepared. Fairly strong spontaneous heating of the mixture was observed, so that it was necessary to cool the flask with water. On conclusion of violent reaction the mixture was heated for 10 hours at the boil in a flask under reflux. The ethyl and butyl alcohols were removed by vacuum distillation on the water bath. The residue on cooling gave crystals, which were washed with ether, dried, and recrystallized from alcohol. The yield of 2-methylcinchoninic acid was 3.6 g (20%), m.p. 240-241°, picrate, m.p. 189-190°.

Literature data: m.p. 240°; picrate, m.p. 190-191° [16].

SUMMARY

1. The synthesis of a number of 2-methylquinolines by the reaction of straight vinyl ethers with aromatic amines was described.

2. The influence of the reaction conditions on the yields of the corresponding quinaldines was investigated.

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* V. M. Demyanovich participated in the synthesis.

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* See Consultants Bureau Translation, page 493.

REACTION OF METAL HALIDE ALCOHOLATES

III. REGULATION OF ORGANOMAGNESIUM REACTIONS

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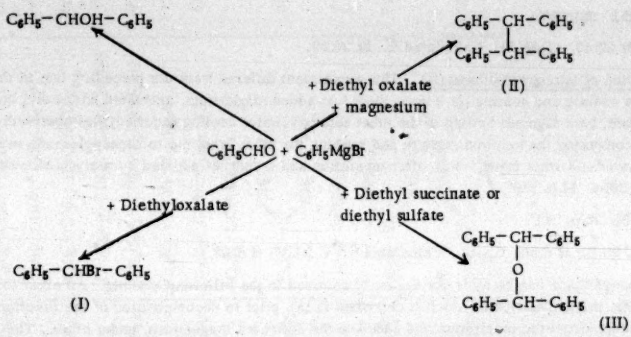
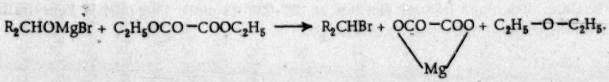
As was shown earlier [1, 2], the magnesium halide carbinolates of diarylcarbinols under the influence of esters are transformed into various compounds depending on the nature of the esters. Inasmuch as the magnesium halide carbinolates are the final products of many organomagnesium reactions, this circumstance makes it possible, using the method of adding a third component, to obtain compounds of a different nature from those usually obtained. A similar possibility of regulating organomagnesium reactions was verified on the example of the reaction of benzaldehyde with phenylmagnesium bromide. As is known, the reaction of these substances leads to the formation of benzhydrol, in which connection this aromatic alcohol is found in the reaction mixture in the form of the magnesium bromide benzhydrolate. The addition of various esters changes the nature of the final products.

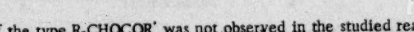


As regards the mechanism of the formation of the halides in the reaction of magnesium halide diarylcarbinolates with esters, leaving this question for future studies, we tentatively depict the reaction by the following scheme:



The formation of symmetrical tetraphenylethane is undoubtedly explained by a Wurtz type of reaction between benzhydryl bromide and metallic magnesium, which fact is also confirmed by experimental data [3].

The retarded formation of diarylmethyl halides in the action of diethyl succinate or diethyl sulfate on magnesium halide diarylcarbinolates serves as the reason for the formation of ethers. The formation of these compounds can be depicted by the usual scheme:



The formation of esters of the type $R_2CHOCOR'$ was not observed in the studied reactions.

Complications in carrying out the above-indicated reactions were observed only in the last reaction – the reaction of forming the ethers. Although the dibenzhydryl ether is obtained in high yield, nevertheless the chance excess of benzaldehyde or phenylmagnesium bromide in the reaction mixture, both capable of reacting with the

diethyl succinate, serves as a reason for the appearance of impurities, which contaminate the obtained ether and interfere with its crystallization. Thes complications can be eliminated and pure dibenzhydryl ether can be obtained if the diethyl succinate is replaced by anhydrous oxalic acid. The possibility of a similar control was also demonstrated in the other reactions, the results of which are given in the table.

In contrast to the diarylcarbinolates, the dialkylarylcarbinolates under the influence of ethyl formate or diethyl oxalate are converted into unsaturated hydrocarbons.

EXPERIMENTAL

Regulation of the Reaction of Benzaldehyde with Phenylmagnesium Bromide

a) Preparation of benzhydryl bromide (I). To an ether solution of benzaldehyde (21.2 g) was added an ether solution of phenylmagnesium bromide, prepared from bromobenzene (31.4 g), and separated from excess magnesium. To the reaction mixture after heating for 5 minutes was added the diethyl ester of oxalic acid (29.2 g); the mixture was again heated for 3 hours and then decomposed with 10% acetic acid. The ether layer was separated from the water layer, washed with a 10% sodium bicarbonate solution, water (here the magnesium oxalate separated), and dried over calcined Na_2SO_4. After distilling off the solvent the substance was vacuum distilled at 4 mm: 1st fraction 68-130°, 10.5 g; 2nd fraction 130-160°, 42 g; residue 2 g. A second distillation of the 2nd fraction gave 38 g (76%) of benzhydryl bromide with b.p. 133-135° (3 mm). After one recrystallization from petroleum ether the substance had m.p. 36-37°.

Literature [5]: m.p. 45°.

Found %: Br 32.40. $C_{13}H_{11}Br$. Calculated %: Br 32.39.

b) Preparation of tetraphenylethane (II). This experiment differed from the preceding one in that after adding the diethyl oxalate and heating for 3 hours there was added magnesium, activated with ethyl bromide, to the reaction mixture; here vigorous boiling of the ether solution (water cooling required) was observed, which soon ceased. After decomposing the reaction mixture and washing the ether layer the tetraphenylethane separated at the interface of the water and ether layer, and after separation and drying was purified by recrystallization from toluene. Yield 12 g (36%). M.p. 210°.

Literature [5]: m.p. 211°.

Found %: C 93.20; H 6.56. $C_{26}H_{22}$. Calculated %: C 93.37; H 6.63.

The tetraphenylethane can be more conveniently obtained in the following manner. An ether solution of benzhydryl bromide, the preparation of which is described in (a), prior to decomposition of the reaction mixture with water, is decanted from the precipitate and added to the activated magnesium, under ether. The remainder of the reaction and the treatment of the mixture are as indicated above. The yield of (II) is increased to 16.7 g (50%).

c) Preparation of dibenzhydryl ether (III). In contrast to Experiment (a) anhydrous oxalic acid (9 g) was taken instead of diethyl oxalate. The main fraction distilled at 190-230° (3 mm), 17 g (40%). Recrystallization from petroleum ether gave dibenzhydryl ether with m.p. 106-107°.

Literature [4]: m.p. 109-110°.

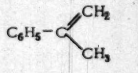
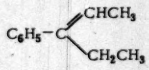
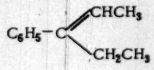
Found %: C 88.89; H 6.25. $C_{26}H_{22}O$. Calculated %: C 89.11; H 6.33.

Regulation of Organomagnesium Reactions

The diarylcarbinols, and also the dialkylarylcarbinols were synthesized under the usual Grignard reaction conditions. A change in the nature of the reaction was produced by adding various esters, indicated in the Table. Further treatment of the reaction mixture and the methods for the isolation of the diarylmethyl bromides, and also the unsaturated hydrocarbons, are indicated above.

SUMMARY

Methods have been described for the regulation of certain organomagnesium reactions, making it possible to obtain instead of the diarylcarbinol one of three products: the diarylmethyl halide, the symmetrical tetraarylethane or the diarylmethyl ether, and instead of the dialkylarylcarbinol – the unsaturated hydrocarbon.

Experiment No.	Reaction Components			Formula of obtained product	Yield (%)	Boiling point or melting point	
	I	II	III			Experiment data	Literature data
1	C_6H_5CHO	o-$CH_3C_6H_4MgBr$	–	$C_6H_5-CHOH-C_6H_4CH_3$ (o)	–	–	–
2	C_6H_5CHO	o-$CH_3C_6H_4MgBr$	$(COOC_2H_5)_2$	$C_6H_5-CHBr-C_6H_4CH_3$ (o)	60	136-138° (3 mm)	–
3	C_6H_5CHO	p-$CH_3C_6H_4MgBr$	–	$C_6H_5-CHOH-C_6H_4CH_3$ (p)	–	–	–
4	C_6H_5CHO	p-$CH_3C_6H_4MgBr$	$(COOC_2H_5)_2$	$C_6H_5-CHBr-C_6H_4CH_3$ (p)	55	135-137 (3 mm)	190-200 (15 mm) [7]
5	$HCOOC_2H_5$	o-$CH_3C_6H_4MgBr$	–	$CH_3C_6H_4-CHOH-C_6H_4CH_3$ (o)	–	119-120 m.p.	119.5 m.p. [6]
6	$HCOOC_2H_5$	o-$CH_3C_6H_4MgBr$	$(COOC_2H_5)_2$	$CH_3C_6H_4-CHBr-C_6H_4CH_3$ (o)	45	66 m.p.	66-67 [1]
7	$HCOOC_2H_5$	α-$C_{10}H_7MgBr$	–	$C_{10}H_7-CHOH-C_{10}H_7$ (α)	–	145-146 m.p.	146-147 m.p. [4]
8	$HCOOC_2H_5$	α-$C_{10}H_7MgBr$	$HCOOC_2H_5$	$C_{10}H_7-CHBr-C_{10}H_7$ (α)	52	181-182 m.p.	181-182 m.p. [5]
9	CH_3COCH_3	C_6H_5MgBr	–	$C_6H_5-COH(CH_3)_2$	–	197 (761 mm)	202 [4]
10	CH_3COCH_3	C_6H_5MgBr	$HCOOC_2H_5$		70	158-161 (752 mm)	158-160 (748 mm) [5]
11	$C_6H_5COOC_2H_5$	C_2H_5MgBr	–	$C_6H_5-COH(C_2H_5)_2$	–	224 (746 mm)	223-224 (762 mm) [4]
12	$C_6H_5COOC_2H_5$	C_2H_5MgBr	$HCOOC_2H_5$		75	196-198 (751 mm)	197-198 (753 mm) [5]
13	$C_6H_5COOC_2H_5$	C_2H_5MgBr	$(COOC_2H_5)_2$		75	196-198 (751 mm)	197-198 (756 mm) [5]

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* See Consultants Bureau Translation, page 281.

** See Consultants Bureau Translation, page 505.

CHEMICAL STRUCTURE AND PARASITICIDAL ACTIVITY

XVIII. SUBSTITUTED BENZYLDIETHYLAMINES

V. I. Stavrovskaya

Aminobenzyldiethylamines and their substituted derivatives were needed for the synthesis of anti-malarial compounds of the acridine and quinoline series with lateral cyclic substituents [1, 2, 3]. Of the ten compounds synthesized by us near the beginning of our work, three were described in the literature: o-, m-, and p-benzyl diethylamines.

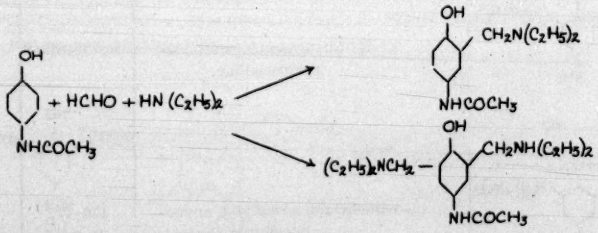
The p-, o-, and m-benzyldiethylamines, which were needed for condensation (Nos. 1, 2, 3 in the table) were obtained from the corresponding nitrobenzyl chlorides by their interaction with diethylamine, and the subsequent reduction of the nitro-group [4, 5].

2-Hydroxy-5-aminobenzyldiethylamine (No. 4) was synthesized by the reduction of the corresponding nitro-compound, which we obtained by the Mannich reaction from p-nitrophenol, formaldehyde, and diethylamine, analogously to the synthesis of diethylaminophenols [6]. Regardless of the various changes in the conditions under which the Mannich reaction was carried out, including changes in the temperature and heating time, the excess of diethylamine, the use of the latter in the form of a base or a hydrochloride, or changes in the method of treatment of the reaction mixture which is obtained, the maximum yield of the product was 38%. In the work published by Burckhalter [7], the yield of 2-hydroxy-5-nitrobenzyldiethylamine, prepared by this method, is given as 40%.

On the reduction of the synthesized 2-hydroxy-5-nitrobenzhyldiethylamine with iron, in a neutral medium, 2-hydroxy-5-aminobenzyldiethylamine was obtained; attempts to vacuum distil the product led to its decomposition.

2-Methoxy-5-aminobenzyldiethylamine (No. 5) was prepared by the reduction of the corresponding 5-nitro-compound, which, in its turn, was synthesized from 2-methoxy-5-nitrobenzyl chloride and diethylamine.

3,5-Bis-(diethylaminomethyl)-4-hydroxyaniline (No. 6) was synthesized by the Mannich reaction from 3-diethylamino-4-hydroxyacetanilide, or directly from p-acetoaminophenol, formaldehyde, and diethylamine, with the subsequent saponification of the aceto group. When the second method is used, it is necessary to take a five or six-fold excess of diethylamine in order to increase the yield; if this is not done, a considerable quantity of 3-diethylaminomethyl-4-hydroxyacetanilide is formed (Mannich's monobase).



The separation of the mixture of 3,5-bis-(diethylaminomethyl)-4-hydroxyacetanilide and 3-diethylaminomethyl-4-hydroxyacetanilide was carried out by their different solubilities in ether. While 3,5-bis-(diethylaminomethyl)-5-hydroxyacetanilide is quite soluble in ether, 3-diethylaminomethyl-4-hydroxyacetanilide is almost insoluble in it. The latter circumstance is probably caused by possible internal salt formation between the

TABLE

Aminoalkylarylamines

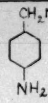
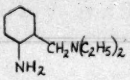
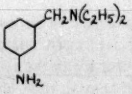
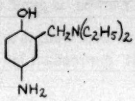
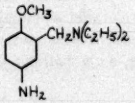
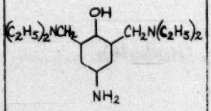
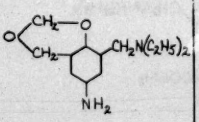
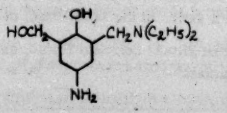
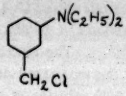
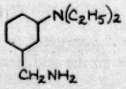
No.	Formula	Name	Temperature	
			of boiling of the base	of melting of the hydrochloride
1	2	3	4	5
1		p-Aminobenzyldiethylamine	100-101° (1 mm)	230-231°
2		o-Aminobenzyldiethylamine	103-104 (5 mm)	186-187
3		m-Aminobenzyldiethylamine	118-120 (3 mm)	222-223
4		2-Hydroxy-5-aminobenzyldiethylamine	Not distilled	Oxalate 172-172.5
5		2-Methoxy-5-aminobenzyldiethylamine	137-138 (2 mm)	Picrate 149.5-150
6		3,5-Bis-(diethylaminomethyl)-4-hydroxyaniline	Not distilled	Picrate 187
7		3-Diethylaminomethyl-4-amino-saligeninmethylenic ether	170-172 (2 mm)	208-210

TABLE (continued)

1	2	3	4	5
8		3-Diethylaminomethyl-5-amino-saligenin	Not purified	
9		m-Diethylaminobenzyl chloride	120 (3 mm)	204, picrate 111-112
10		m-Diethylaminobenzylamine	122-123 (2-2.5 mm)	240 (decomposition), picrate 145-146

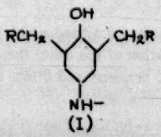
acid hydroxy group and the basic diethylamino group. This hypothesis finds confirmation in the existence of the salts of o-nitrophenol with methylamine and other amines [8, 9].

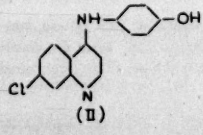
3-Diethylaminomethyl-5-aminosaligeninmethylinic ether (No. 7) was prepared by the reduction of the corresponding nitro-compound with iron in an acid medium.

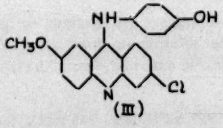
3-Diethylaminomethyl-5-aminosaligenin (No. 8), was synthesized by the same method from 3-diethylaminomethyl-5-nitrosaligenin.

We also obtained aliphatic-aromatic amines of a somewhat different structure, namely: m-diethylaminobenzyl chloride (No. 9) and m-diethylaminobenzylamine (No. 10). The syntheses of these compounds have been described in detail earlier [10].

Later, on the synthesis of acridine and quinoline compounds with more complex lateral cyclic substituents [e.g., type (I)], where R equals cyclohexylamino-, anilino-, or α-methylpyrrolidine groups, we did not synthesize aromatic amines of this structure, but obtained the required end products by the Mannich reaction from 7-chloro-(4.4'-hydroxyphenyl)-aminoquinoline (II) or from 2-methoxy-6-chloro-(4'-hydroxyphenyl)-aminoacridine (III), formaldehyde, and the corresponding amine [11].


(I)


(II)


(III)

Although lateral cyclic substituents with cyclohexylamine, aniline, and α-methylpyrrolidine were introduced in the quinoline and acridine rings, these aromatic amines will not be described.

EXPERIMENTAL

m-Aminobenzyldiethylamine was prepared by the reduction of m-nitrobenzyldiethylamine with iron in a neutral medium, or by catalytic reduction over a nickel catalyst, with a yield, in the latter case, of 88%.

m-Aminobenzyldiethylamine distilled at 118-120° (3 mm); it is an almost colorless liquid, quite soluble in alcohol, ether, benzene, and acids; it is insoluble in water and dilute alkali.

Found %: N 16.60, 16.06. $C_{11}H_{18}N_2$. Calculated %: N 15.73.

2-Hydroxy-5-nitrobenzyldiethylamine. In a three-necked flask, equipped with a reflux condenser, a stirrer, a thermometer and a dropping funnel, was placed 23.2 g of p-nitrophenol; diethylamine (13.4 g) was added by drops, at a rate so that the temperature did not rise above 20°. Then formalin was added (17 g, 38%), whereupon the mixture was gradually diluted, stirred 15 minutes at room temperature, 2 hours at 80°. The obtained liquid reaction mixture was heated over a water bath at 80° (13-14 mm) in order to drive off the unreacted diethylamine and formaldehyde. The thick red oil which remained (31.2 g) was treated with a 10% solution of hydrochloric acid. The white hydrochloride which was formed was dissolved in 100 ml of water and was extracted with ether several times in order to drive off the unreacted p-nitrophenol. The aqueous solution of the hydrochloride was saturated with potash; the base which precipitated was extracted with ether. The ether solution was dried with potash.

After the ether was distilled off, 15 g remained of a red liquid, which was converted to the hydrochloride by the treatment of the base with alcoholic HCl. The hydrochloride was isolated on the addition of ether, and was crystallized from a 10% hydrochloric acid solution, or from alcohol.

The hydrochloride melts at 223-224° (decomposition), which corresponds to the literature data [7]. The hydrochloride is quite soluble in water, giving a yellowish coloration to the solution; it is soluble in alcohol, and in dilute acids; it is insoluble in acetone and ether.

Found %: N 10.86, 10.85. $C_{11}H_{17}O_3N_2Cl$. Calculated %: N 10.75.

The base 2-hydroxy-5-nitrobenzyldiethylamine was prepared by the dissolution of the hydrochloride in water and the subsequent saturation of the solution with potash. The base is a solid substance of a bright yellow color, quite soluble in water, alcohol, benzene, dilute acids and alkalis. It was crystallized from water in the form of plates: m.p. 87°.

6.188 mg sub.: 0.706 ml N_2 (20°, 726 mm). 4.000 mg sub.: 0.461 ml N_2 (20°, 726 mm). Found %: N 12.70, 12.83. $C_{11}H_{16}O_3N_2$. Calculated %: N 12.50.

2-Hydroxy-5-aminobenzyldiethylamine. A three-necked flask, equipped with a reflux condenser, a stirrer, and a dropping funnel, was charged with 9 g of cast iron filings and 20 ml of water. 8 ml of concentrated HCl was then introduced, by drops with heating and stirring, after which 10.2 g of 2-hydroxy-5-nitrobenzyldiethylamine was added by small portions over a period of 30 minutes. The stirring and heating were carried out for one more hour; after which the liquid was cooled, alkalized with potash, and filtered from the residue; the latter was washed several times with ether. The filtrate was extracted with ether; the ether solution was dried with sodium sulfate. After the ether was distilled off there remained 7 g of a thick, dark liquid. On the attempt to distil the substance in vacuum, it decomposed. The oxalate was obtained by the decantation of the ether solution of the base (1.94 g) and an alcoholic solution of oxalic acid (0.9 g); the oxalate was crystallized from aqueous acetone. M.p. 172-172.5° (decomposition). The oxalate is quite soluble in water, soluble in alcohol, and insoluble in ether and acetone.

5.685 mg sub.: 0.500 ml N_2 (21°, 741 mm). 5.700 mg sub.: 0.500 ml N_2 (24°, 746 mm). Found %: N 9.96, 9.87. $C_{13}H_{20}O_5N_2$. Calculated %: N 9.86.

From an aqueous solution of the oxalate, on its saturation with potash, was isolated a base which was extracted with ether. The ether solution was dried with sodium sulfate. After the distillation of the ether there remained an oil which quickly became dark in the air. The base is soluble in alcohol, ether, benzene and dilute alkalis and acids.

5.014 mg sub.: 0.627 ml N_2 (22°, 746 mm). Found %: N 14.20. $C_{11}H_{18}ON_2$. Calculated %: N 14.43.

2-Methoxy-5-aminobenzyldiethylamine was obtained by the reduction of the corresponding nitro-product with iron, in a neutral medium. The method of work was the same as in the experiment on the preparation of 2-hydroxy-5-aminobenzyldiethylamine.

The reddish-oil which remained after the ether was driven off distilled at 137-138° (2 mm). From 7.3 g of the original nitro-compound was obtained 4.6 g (72%) of a new substance. The yellowish, mobile liquid is soluble in ether, alcohol, benzene and acids; it is insoluble in water and alkalis. It darkens quickly in the air.

4.648 g sub.: 0.549 ml N_2 (24°, 753 mm). 5.051 mg sub.: 0.598 ml N_2 (24°, 747 mm). Found %: N 13.45, 13.47. $C_{12}H_{20}ON_2$. Calculated %: N 13.45.

3,5-Bis-(diethylaminomethyl)-4-hydroxyacetanilide. a) 3-Diethylaminomethyl-4-hydroxyacetanilide (23.6 g), diethylamine (10 ml), formalin (10 ml, 35%), and alcohol (25 ml) were heated over a water bath for 6 hours at the boiling point of the liquid within the flask. The alcohol, and the diethylamine which had not reacted, were distilled off. The thick mixture which remained was dissolved in ether at room temperature, and the solution was filtered from the 3-diethylaminomethyl-4-hydroxyacetanilide (5.2 g) which did not enter into the reaction. The ether solution was dried with potash; after the solvent was driven off, the residue was again worked with ether, whereupon a small amount of 3-diethylaminomethyl-4-hydroxyacetanilide was isolated. After the distillation of the ether there remained 25.3 g (80.6%) of a very thick, slightly mobile, yellowish substance, which did not solidify on being allowed to stand for a long time in a vacuum exsiccator. The picrate was yellow in color, and was crystallized from alcohol: m.p. 161-162°.

2.817 mg sub.: 0.421 ml N_2 (23°, 748 mm). 3.028 mg sub.: 0.451 ml N_2 (23°, 749 mm). Found %: N 16.96, 16.93. $C_{36}H_{49}O_{23}N_{12}$. Calculated %: N 16.97.

b) p-Acetaminophenol (7.6 g), formalin (11 ml, 35%), diethylamine (40 ml), and alcohol (20 ml) were heated over a water bath for 11 hours at the boiling point of the liquid within the flask. The further working was as in Experiment (a). After the distillation of the ether, there remained 15 g (94%) of 3,5-bis-(diethylaminomethyl)-4-hydroxyacetanilide.

3,5-Bis-(diethylaminomethyl)-4-hydroxyaniline. 3,5-Bis-(diethylaminomethyl)-4-hydroxyacetanilide (6.4 g) was boiled with 20% hydrochloric acid (20 ml) for three hours. The solution was alkalized with potash and extracted with ether. The ether solution was washed with water and dried with sodium sulfate. After driving off of the solvent, there remained 4.5 g (80%) of a thick brown liquid, which did not distil in a vacuum.

The picrate was yellow in color, and was crystallized from aqueous acetone in the form of small needles, which were conglomerated into nodules; m.p. 187°.

2.601 mg sub.: 0.402 ml N_2 (22°, 744 mm). 3.804 mg sub.: 0.588 ml N_2 (22°, 744 mm). Found %: N 17.51, 17.51. $C_{24}H_{33}O_{22}N_{12}$. Calculated %: N 17.39.

The base, which was isolated from the picrate, is a thick yellow liquid. The base is very soluble in alcohol, ether, acetone, benzene, and dilute acids and bases; it is slightly soluble in water. Its water-alcohol solution gives a red-brown coloration with ferric chloride.

2.840 mg sub.: 0.382 ml N_2 (21°, 737 mm). 2.446 mg sub.: 0.333 ml N_2 (22°, 737 mm). Found %: N 15.14, 15.28. $C_{16}H_{29}ON_3$. Calculated %: N 15.05.

3-Diethylaminomethyl-5-aminosaligeninmethylinic ether was prepared by the reduction of 5-nitro-saligeninmethylenic ether with iron in hydrochloric acid, with a yield of 67%. The thick, dark liquid which was left after the driving off of the ether, was distilled at 170-172° (2 mm). The base is a thick, colorless liquid, which is quite soluble in ether, benzene, alcohol, and dilute acids; it is insoluble in water and bases.

4.300 mg sub.: 0.441 ml N_2 (20°, 767 mm). 5.444 mg sub.: 0.549 ml N_2 (20°, 767 mm). Found %: N 12.06, 11.86. $C_{13}H_{20}O_2N_2$. Calculated %: N 11.86.

The hydrochloride is white in color and is crystallized from a mixture of alcohol with ether; m.p. 208-210°.

3.230 mg sub.: 0.255 ml N_2 (21°, 768 mm). 3.368 mg sub.: 0.265 ml N_2 (19°, 768 mm). Found %: N 9.26, 9.29. $C_{13}H_{22}O_2N_2Cl_2$. Calculated %: N 9.06.

3-Diethylaminomethyl-5-aminosaligenin was prepared by reduction with iron in an acid medium. From 6 g of the original nitro-compound was obtained 2.5 g of a thick liquid, which was used without purification in the subsequent condensation reaction with the acridine and quinoline rings. The hydrochloride of 3-diethylaminomethyl-5-aminosaligenin is a sticky mass, which did not solidify on purification and long standing in a vacuum-exsiccator.

SUMMARY

A number of aromatic amines – substituted aminobenzyldiethylamines – have been synthesized and characterized.

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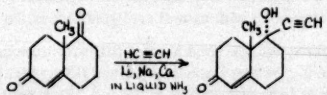
* See Consultants Bureau Translation, page 999.
** See Consultants Bureau Translation, pages 313, 319.
*** See Consultants Bureau Translation, page 787.
**** See Consultants Bureau Translation, page 1897.

SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

XXVIII. THE CONDENSATION OF ACETYLENE WITH 9-METHYL-1,6-DIKETO-Δ^5-OCTAHYDRONAPHTHALENE. THE SYNTHESIS AND TRANSFORMATIONS OF 9-METHYL-1-ETHINYL-1-HYDROXY-6-KETO-Δ^5-OCTAHYDRONAPHTHALENE

I. N. Nazarov and I. A. Gurvich

In our preceding communications we described the preparation of a number of bicyclic acetylenic alcohols, and the synthesis of steroid compounds and their analogs [1] on the basis of these bicyclic compounds. From this point of view the synthesis of the acetylenic alcohol (II) from the diketooctalene (I), which is accessible, is of great interest; the method of preparation of the diketooctalene was worked out in our laboratory, using resorcin as a starting material [2]. In 1951 a short article [3] was published on the synthesis of the acetylenic alcohol (II) by the condensation of sodium acetylide with the diketone (I) in liquid ammonia. However, the authors later reported that they had obtained, not the separate compound, but a mixture of substances [4]. The detailed study which we carried out on the condensation of acetylene with 9-methyl-1,6-diketo-Δ^5-octahydronaphthalene (I) showed that this reaction goes best when it is carried out in a solution of liquid ammonia and lithium acetylide; in this case pure, crystalline 9-methyl-1-ethinyl-1-hydroxy-6-keto-Δ^5-octahydronaphthalene (II) is obtained with a yield of 70%.



(I) (II)

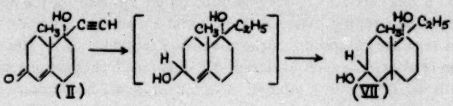
This condensation was also carried out with the acetylides of calcium and sodium; in the latter case the results were difficult to reproduce and the yield of the acetylenic alcohol (II) in the best experiments constituted only 50%. In order to obtain high yields of the crystalline acetylenic alcohol (II) it is necessary carefully to follow the method of synthesis described in the experimental section of this paper. Deviation from the method used, especially in the case of the use of sodium acetylide, leads to the formation of tar, or to the obtaining of a liquid mixture of products of indeterminate structure, with which, evidently, the previous authors had to deal. The use of other condensing agents, including potassium alcoholates and pulverized potassium hydroxide under the pressure of acetylene [5], as well as acetylene magnesium halides, did not give positive results. In the literature there are indications of the successful use of lithium and potassium acetylides in the synthesis of acetylenic alcohols from α,β-unsaturated ketones [6]. Recently, papers have also appeared on the use of lithium acetylide for the synthesis of acetylenic alcohols from certain aliphatic-aromatic ketones, and from the enolic ester of methyldihydroresorcin [7].

Unlike a number of α,β-unsaturated ketones, the diketone (I) enters into a condensation reaction with acetylene only with an unconnected ketone group. This is confirmed by the presence of an α,β-unsaturated group in the acetylenic alcohol (II), which is shown by its ultraviolet absorption spectrum. The acetylenic ketone alcohol (II) forms the dark 2,4-dinitrophenylhydrazone. The hydrogenation of the acetylenic alcohol (II) in dioxan in the presence of a Pd catalyst goes selectively, and after the absorption of one mole of hydrogen, the vinyl ketone alcohol (III) is formed with a yield of 93%; this compound gives the bright red 2,4-dinitrophenylhydrazone.

If the hydrogenation of acetylenic alcohol (II) is carried out under the same conditions until the sudden deceleration of the absorption of hydrogen, the ethyl ketone alcohol (IV) is formed with a yield of 75%; this substance gives 2,4-dinitrophenylhydrazone that is reddish in color. The ultraviolet absorption spectrum of the compound confirms the presence in alcohol (IV) of an α,β-unsaturated ketone group.

The presence of double bonds, connected with ketone groups in ketone alcohols (II, III and IV) is also confirmed by the ultraviolet absorption spectra taken from their 2,4-dinitrophenylhydrazones, and by the red coloration of the latter, which is characteristic for these derivatives of α,β-unsaturated ketones. On the hydrogenation of the hydroxyoctalone (IV) in ethyl alcohol, in the presence of a Pd catalyst, a mixture of two stereo-isomers of hydroxydecalone,(V) and (VI) are formed; they were characterized as 2,4-dinitrophenylhydrazones.

The isomerism of the obtained hydroxydecalones (V) and (VI) may be explained only by differences in the spatial position of the angular hydrogen at C_9, that is, one of them is a derivative of cis-decalin and the other a derivative of trans-decalin. Neither hydroxydecalone (V) or (VI) was hydrogenated in alcoholic solutions in the presence of platinum dioxide. However, on the hydrogenation of the original acetylenic alcohol (II), under these same conditions, the ketone group in it was also affected, as a consequence of which a mixture of substances was formed. Thus, on the exhaustive hydrogenation of the acetylenic alcohol (II) in an alcoholic solution, in the presence of platinum dioxide, the diol (VII) belonging to the trans-decalin series was isolated along with the hydroxyketone (VI). It is necessary to assume that the diol (VII) is formed through an intermediate unsaturated alcohol of the octalene series (shown in brackets), which was not isolated by us.



(II) (VII)

On the oxidation of the diol (VII) with chromium trioxide in glacial acetic acid, the trans-hydroxydecalone (V) was obtained.

Recently, there have appeared in the literature indications of the successful reduction with lithium in liquid ammonia of Δ^8-11-ketosteroids to 11-ketosteroids with natural configurations at the eighth and ninth carbon atoms [8].

We reduced the acetylenic alcohol (II) and the vinyl alcohol (III) with lithium in liquid ammonia and obtained (with yields of 50 and 65%) the corresponding ketone alcohols (VIII) and (IX), which belong to the trans-decalin series. The 2,4-dinitrophenylhydrazones of hydroxydecalones (VIII) and (IX), as well as the 2,4-dinitrophenylhydrazones of hydroxydecalones (V) and (VI), have a yellow coloration, which is characteristic for ketones with isolated carbonyl groups.

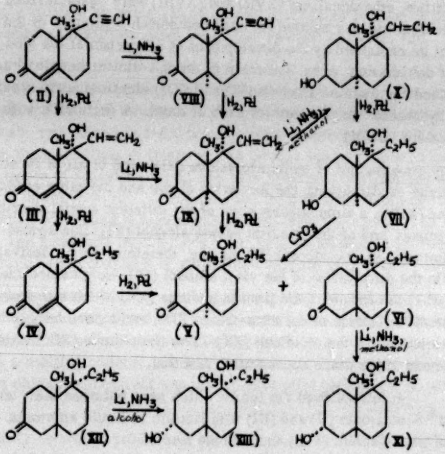
On the exhaustive hydrogenation of ketone alcohols (VIII) and (IX) in alcoholic solutions, the same trans-ethylhydroxydecalone (V) was obtained.

On the reduction of the vinyl ketone alcohol (III) with lithium in liquid ammonia, in the presence of methanol, trans-vinyldecalindiol (X) was obtained; on the hydrogenation of this compound, the above-described trans-ethyldecalindiol (VII)* was formed. On the reduction of cis-ethylhydroxydecalone (VI) with lithium in liquid ammonia, in the presence of methanol, cis-ethyldecalindiol (XI) was obtained.

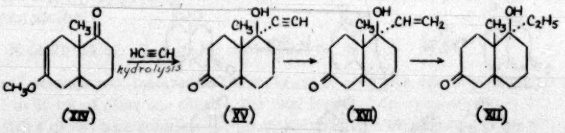
From cis-ethylhydroxydecalone (XII), which was prepared earlier in our laboratory [1], and which is isomeric with hydroxydecalones (V) and (VI), we obtained another cis-ethyldecalindiol (XIII); the new compound was prepared by the reduction of cis-ethylhydroxydecalone with lithium in liquid ammonia in the presence of alcohol; the yield was quantitative.

The reduction of the double bonds in compounds (II) and (III) with lithium in liquid ammonia, and also the formation of the two isomeric hydroxydecalones (V) and (VI) from ketone alcohol (IV) on hydrogenation, is a confirmation of the spectroscopic data on the presence of a double bond connected with a ketone group in the acetylenic ketone alcohol (II) and also in ketone alcohols (III) and (IV).

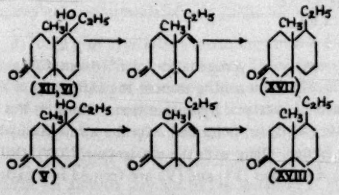
* The spatial position of the hydroxy-group in position 6 in diols (VII), (X), (XI) and (XIII) is assumed by analogy with the configurations of 3-hydroxysteroids, obtained by the reduction of 3-ketosteroids.



However, all of the ketone alcohols of the decalin series (V, VI, VIII, IX) which were obtained from these unsaturated alcohols, turned out to be substances which differed from the corresponding isomeric derivatives of cis-decalin which were obtained earlier [1].



The fact that ketone alcohol (VI) proved to be different from (XII), although they are both derivatives of cis-decalin, indicates that there is a difference in the spatial position of the substituent at the first hydrocarbon atom in these compounds, and therefore, also in the original acetylenic alcohols (II) and (XV), and, correspondingly, in all other compounds obtained from them.



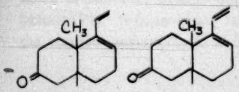
Thus, the addition of acetylene to the carbonyl group at the first position of diketooctalene (I) and methoxyketooctalene (XIV) takes place in a way that is spatially different.

Other 9-methyl-1-octalones, and also 17-keto-steroids, are condensed with acetylene similarly to methoxyoctalone (XIV), forming the corresponding acetylenic alcohols, in which the acetylene radical occupies the trans-position in relation to the angular methyl group. Unlike these ketones, diketooctalene (I) was condensed with acetylene in such a way that in the acetylenic alcohol (II) which was formed, the ethinyl group was in the cis-position in relation to the angular methyl group. This kind of spatial position is occupied, as is known, by the side chain at C_{17} in all natural steroids. These facts are of considerable interest in connection with the stero chemistry of cyclic compounds.

In order to make clear which of the ketone alcohols (V) or (VI), is a derivative of cis-decalin, all three hydroxydecalones (V, VI and XII) were subjected to dehydration with p-toluenesulfonic acid, and subsequently to hydrogenation with platinum, to the corresponding ethyldecalones.

In view of the small quantities, ethyldecalones (XVII) and (XVIII) were characterized by their crystalline derivatives. In all cases one semicarbazone was isolated for each compound; a mixture of 2,4-dinitrophenylhydrazones was obtained, which might be explained by the development of isomerism at the first carbon atom during the hydrogenation of the products of dehydration, or by isomerism of the 2,4-dinitrophenylhydrazones themselves. For cis-ethyldecalones (XVII), obtained from ketone alcohols (VI) and (XII) identical semicarbazones were obtained, and the same 2,4-dinitrophenylhydrazone was obtained for each of them. A derivative with a higher melting point was obtained from the trans-decalone (XVIII).

In view of the fact that the cis-structure of methoxyoctalone (XIV) and of all of its derivatives, follows from the method of its preparation (diene condensation), the formation of one and the same ethyldecalone (XVII) from isomeric ketone alcohols (VI) and (XII) is a simultaneous proof of the different spatial distribution of the substituents at the first carbon in these compounds, and of the fact that ketone alcohol (VI), like ketone alcohol (XII), belongs to the cis-decalin series. The isomeric ketone alcohol (V) may be, therefore, only a derivative of trans-decalin.

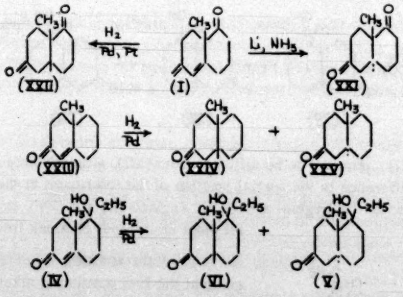


(XIX) (XX)

On the dehydration of the vinyl alcohol (IX), we obtained the crystalline trans-diene (XIX) in contrast to the liquid cis-diene (XX) which was described earlier [1]. The semi-carbazone of the trans-diene (XIX) melts considerably higher than the semi-carbazone of the cis-diene (XX). The trans-diene (XIX) which was obtained, easily enters into a diene condensation reaction.

It follows from the results which were obtained that on the reduction of Δ^5-6-octalones (II) and (III) with lithium in liquid ammonia, only the derivatives of trans-decalin (VIII) and (IX) are formed.

On the reduction of diketooctalene (I) with lithium in liquid ammonia trans-diketodecalin (XXI) was also obtained, but with a yield of only 10%, in view of the instability of the original diketone (I) in an alkaline medium. There are also indications in the literature that on the reduction of Δ^4-3-ketosteroids with lithium in liquid ammonia in the presence of alcohol, compounds with trans-coupling of rings A and B [9] are formed.



In contrast to reduction with lithium in liquid ammonia, the catalytic hydrogenation of Δ^5-6-octalones leads, predominately, to the formation of derivatives of cis-decalin. It is interesting to note the influence of the substituent at the first carbon atom on the spatial directing influence of catalytic hydrogenation. Thus, on the catalytic hydrogenation of diketooctalene (I), only cis-diketodecalin (XXII) [2] is formed. On the catalytic hydrogenation of Δ^5-6-octalone (XXIII), the trans-isomer (XXV) [10] is formed along with the cis-isomer (XXIV). On hydrogenation of ketone alcohol (IV), as indicated above, cis- and trans-decalones (VI) and (V) are formed in a ratio of 7:5.

The acetylenic alcohol (II) and the trans-vinyl alcohol (IX), in tests for androgenic activity in doses up to 500 γ turned out to be inactive.

EXPERIMENTAL

9-Methyl-1-ethinyl-1-hydroxy-6-keto-Δ^5-octahydronaphthalene (II). In all the experiments, ammonia which had previously been distilled through a column containing solid potassium hydroxide was used. The acetylene had been preliminarily purified by being passed through a saturated solution of sodium bisulfite, then through a chromic mixture, and dried with sulfuric acid, soda lime, calcium chloride, and passed through a column containing silica gel.

a) A four-necked, round-bottomed flask, with a volume of about two liters, equipped with a thermometer, a gas-intake tube, a dropping funnel, a mechanical stirrer with a mercury seal and a gas-outlet, connected with a tube filled with solid alkali, was placed in a dry ice and acetone bath (−70°). 0.5 liter of dry liquid ammonia was distilled in the flask, and then two liters of finely ground lithium was gradually added with stirring; while the lithium was being added a stream of acetylene which had been previously purified and dried was passed through the reaction vessel. After full decolorization of the solution, 25 g of diketooctalene (I) with a m.p. of 50-50.5° [2] in 400 ml of anhydrous ether was added with energetic stirring over the course of an hour. The mixing and the passing of the acetylene were continued for 3.5 hours more, with cooling down to −70°, after which the reaction mixture was decanted into a solution of 20 g of ammonium chloride in 150 ml of water.

The ether layer was separated, and the crystals of acetylenic alcohol which were isolated, were dissolved in chloroform. Both solutions were neutralized with solid carbonic acid, washed with water and dried with sodium sulfate. After the distillation of the solvent and recrystallization from ethyl acetate, 15 g of the colorless acetylenic alcohol crystals (II) with a melting point of 170-171° was obtained. The water-ammonia solution was extracted with chloroform, and the chloroform extract was treated with solid carbonic acid, washed with water and dried with sodium sulfate.

7.3 g more of slightly colored crystals were obtained; from these crystals, after repeated recrystallizations from ethyl acetate, 5 g of colorless crystals with a melting point of 170-171° were isolated. 20 g (70%) of the pure acetylenic alcohol (II) was obtained in all.

Further crystallization gave an alcohol with a melting point of 171.5-172.5°. The absorption spectrum: $\lambda_{max.}$ (in methanol) 310 mμ (ϵ = 60), 240 mμ (ϵ = 15000).

Found %: C 76.31, 76.36; H 7.97, 7.82. $C_{13}H_{16}O_2$. Calculated %: C 76.43; H 7.90.

The 2,4-dinitrophenylhydrazone of alcohol (II) is a dark red crystalline substance with a melting point of 217.5-218.5° (from alcohol).

Found %: N 14.32, 14.50. $C_{19}H_{20}O_5N_4$. Calculated %: N 14.57.

b) 0.65 g of calcium was dissolved in 160 ml of liquid ammonia, and after preparation of the acetylide, 2.4 g of diketone (I) in 80 ml of ether was added. The total length of the experiment was five hours. After the ordinary treatment, 1.3 g of the pure colorless acetylenic alcohol (II) with a melting point of 171-172° was obtained.

c) 2.1 g of sodium was dissolved in 90 ml of liquid ammonia and a stream of acetylene was passed through. After decolorization of the solution, a considerable part of the ammonia was distilled off, and after half an hour a solution of 4.8 g of diketone (I) in 80 ml of ether was added. The mixing and the passing of the acetylene through the reaction mixture at −70° was continued for one hour and fifty minutes. Then, 5 g of solid carbonic acid was added and the reaction mixture was poured into 70 ml of a saturated aqueous solution of ammonium chloride. 2.7g of slightly colored crystals of acetylenic alcohol (II) with a melting point of 169-170°* was obtained.

d) 0.02 g of crystalline ferric nitrate and 0.08 g sodium were added to 60 ml of liquid ammonia with stirring. Then, in fifteen minutes 1 g of sodium was added gradually and a stream of acetylene was passed through. After the preparation of the acetylide, a solution of 2.4 g of diketone (I) in 80 ml of ether was added to it with stirring, and with the passage of acetylene through the mixture. After an hour and twenty minutes the mixture was treated as described above. 1.5 g of acetylenic alcohol (II) with a melting point of 169-170° was obtained.

An increase in the relative quantity of acetylide and in the reaction time, as well as the postponement of the treatment for another day, led to the lowering of the yield of the crystalline alcohol (II).

9-Methyl-1-vinyl-1-hydroxy-6-keto-Δ^5-octahydronaphthalene (III). 20.4 g of acetylenic alcohol (II), with a melting point of 171-172° was hydrogenated in 100 ml of dioxan in the presence of 5% palladium on calcium carbonate until the complete disappearance of the reaction for acetylene with an ammonia solution of silver oxide, for

* The crystalline alcohol (II) was first prepared in our laboratory by L. I. Shmonin in experiments with sodium acetylide.

which 2460 ml of hydrogen was needed (17°, 762.5 mm). According to theory, 2365 ml of hydrogen is necessary for the hydrogenation of the triple bond to a double bond. After the solvent was driven off, the substance was completely crystallized and washed with 20 ml of ether. 19.2 g of the vinyl alcohol (III) was isolated; it is a colorless crystalline substance with a melting point of 76.5-77°, is quite soluble in ether, acetone, alcohol, ethyl acetate and benzene.

Found %: C 75.62, 75.63; H 8.76, 8.92. $C_{13}H_{18}O_2$. Calculated %: C 75.69; H 8.80.

The 2,4-dinitrophenylhydrazone of the vinyl alcohol (III) is a red, crystalline substance with a melting point of 167-167.5° (from alcohol). $\lambda_{max.}$ (in isooctane) 369 mμ.

Found %: C 58.73, 58.86; H 5.66, 5.80; N 14.35, 14.37. $C_{19}H_{22}N_4O_5$. Calculated %: C 59.05; H 5.75; N 14.50.

9-Methyl-1-ethyl-1-hydroxy-6-keto-Δ^5-octahydronaphthalene (IV). 2 g of the acetylenic alcohol (II) was hydrogenated in 20 ml of dioxan in the presence of a Pd catalyst, until a sharp deceleration in the rate of the absorption of hydrogen. 590 ml of hydrogen was absorbed (17°, 761 mm) as against 500 ml theoretically necessary for 2 moles of hydrogen. After the partial distillation of the solvent, 1.4 g of crystals with a melting point of 135-136° were obtained. On recrystallization from ethyl acetate and alcohol with ether, pure ethylhydroxyoctalone (IV) was obtained in the form of colorless crystals with a melting point of 139-139.5°. λ_{max} (in methanol), 313 mμ (ϵ = 80) 245 mμ (ϵ = 14800).

Found %: C 74.99, 74.82; H 9.71, 9.67. $C_{13}H_{20}O_2$. Calculated %: C 74.96; H 9.68.

Crystals with a melting point of 106-107° were isolated from the mother liquor; they turned out to be cis-ethylhydroxydecalone (VI) (a mixed sample did not give a depression).

The 2,4-dinitrophenylhydrazone of the octalone (IV) forms crystals that are reddish in color and have a melting point of about 191-192° (with softening at about 110°). $\lambda_{max.}$ (in isooctane) 359, 374 mμ.

Found %: N 14.65, 14.45. $C_{19}H_{24}N_4O_5$. Calculated %: N 14.43.

Cis-9-methyl-1-ethyl-1-hydroxy-6-ketodecahydronaphthalene (VI). 0.02 g of the acetylenic alcohol (II) was exhaustively hydrogenated in a solution of 15 ml of alcohol with a Pd catalyst. About 80 ml of hydrogen (more than 3 molecules) was absorbed. After the solvent was distilled off, we succeeded in isolating crystals of cis-ethylhydroxydecalone (VI) with a melting point of 106.5-107° (from a mixture of ether and petroleum ether).

Found %: C 74.04, 74.24; H 10.50, 10.61. $C_{13}H_{22}O_2$. Calculated %: C 74.20; H 10.54.

The 2,4-dinitrophenylhydrazone of this kerone forms light orange crystals with a melting point of 207-208°.

Found %: N 14.58. $C_{19}H_{26}N_4O_5$. Calculated %: N 14.43.

The oil from the mother solutions was exhaustively hydrogenated in an alcoholic solution in the presence of platinum dioxide. After the distillation of the solvent, crystals of diol (VII) were isolated; their melting point was 154-155° (from a mixture of ether and petroleum ether).

Trans-9-methyl-1-ethyl-1,6-dihydroxydecahydronaphthalene (VII). 0.2 g of the acetylenic alcohol (II) was hydrogenated in an alcoholic solution in the presence of platinum dioxide. 90 ml of hydrogen was absorbed (about 4 molecules). After the distillation of the solvent, and recrystallization from a mixture of ether and petroleum ether, crystals of the saturated diol (VII) with a melting point of 155.5-156° were obtained (in a mixture of residues).

Found %: C 73.33, 73.27; H 11.44, 11.34. $C_{13}H_{24}O_2$. Calculated %: C 73.53; H 11.39.

The diol (VII) was also obtained in small amounts on the hydrogenation of ethylhydroxyoctalone (IV) in an acid medium with platinum.

Trans-9-methyl-1-ethyl-1-hydroxy-6-ketodecahydronaphthalene (V). 0.2 g of the diol (VII) with a melting point of 153-155° was dissolved in 5 ml of glacial acetic acid, and a solution of 0.15 g of chromic anhydride in 7 ml of glacial acetic acid was added. After two days, alcohol was added, the solvent was distilled off and the mixture was treated in the usual way. Trans-ethylhydroxydecalone (V) with a melting point of 105.5-106.5° was obtained from the ether extract.

Found %: C 74.38, 74.55; H 10.49, 10.65. $C_{13}H_{22}O_2$. Calculated %: C 74.20; H 10.54.

A mixed sample with the cis-isomer (VI) (m.p. 106.5-107°) melted at 82-86°.

The 2,4-dinitrophenylhydrazone of ketone alcohol (V) forms gold-colored crystals with a melting point of 205-206° (from alcohol). $\lambda_{max.}$ (in isooctane) 346 mμ.

Found %: N 14.23, 14.34. $C_{19}H_{26}N_4O_5$. Calculated %: N 14.35.

A mixed sample with the 2,4-dinitrophenylhydrazone of the isomeric ketone alcohol (VI) (m.p. 207-208°) melted at 196-197°.

The catalytic hydrogenation of ethylhydroxyoctalone (IV). 1.5 g of the ketone alcohol (IV) with a melting point of 135-136° was hydrogenated in alcohol in the presence of a Pd catalyst. 187 ml of hydrogen (1 mole) was absorbed, and hydrogenation ceased. Fractional crystallization from ether with mechanical separation of the crystals gave 0.07 g of the ketone alcohol (VI) and about 0.05 g of ketone alcohol (V) (in the leftover oil). On the hydrogenation of the ketone alcohol (IV) with platinum in an alcohol solution, in the presence of hydrochloric acid, we succeeded in isolating the diol (VII) and the ketone alcohol (VI). In the residue there was a considerable quantity of oil.

The 2,4-dinitrophenlyhydrazone of cis-9-methyl-1-ethyl-1-hydroxy-6-ketodecahydronaphthalene (XII). From 110 mg of hydroxydecalone (XII) (m.p. 126-127° [1]) we obtained by the usual method the 2,4-dinitrophenylhydrazone with a melting point of 165-165.5°, with preliminary softening at 162° (from alcohol).

Found %: N 14.44, 14.65. $C_{19}H_{26}N_4O_5$. Calculated %: N 14.35.

Cis-9-methyl-1-ethyl-6-ketodecahydronaphthalene (XVII). a)* 2 g of the cis-9-methyl-1-vinyl-6-keto-Δ^1 octahydronaphthalene (XX) [1] was hydrogenated in a solution of 6 ml of ethyl alcohol according to Adams' method. The hydrogenation was completed in forty-five minutes. 470 ml of hydrogen was absorbed (25°, 759 mm) as against 470 ml theoretically necessary. The catalyst was filtered out, the solvent was distilled off under a slight vacuum and the residue was distilled. 1.5 g of cis-decalone (XVII) with a boiling point of 104-105° at 2 mm was obtained; n_D^{25} 1.5010, d_4^{20} 0.9907.

Found %: C 79.85, 79.77; H 11.23, 11.24. $C_{13}H_{22}O$. Calculated %: C 80.35; H 11.41.

The semicarbazone consists of colorless crystals with a melting point of 197-197.5° (from alcohol).

Found %: N 16.80, 16.87. $C_{14}H_{25}ON_3$. Calculated %: N 16.71.

b) A solution of 0.8 g of cis-hydroxyketodecalin (XII) with a melting point of 126-127° [1] in 20 ml of anhydrous toluene was boiled for half an hour, in order to drive off traces of moisture, in a three-necked flask, equipped with a stirrer, with a mercury seal and a water trap with a reflux condenser. After the cooling of the solution, 24 mg of p-toluenesulfonic acid and about 20 mg of pyrogallol were added to it. Then, the mixture was boiled for an hour with stirring, whereupon moisture appeared in the water trap at once and quickly disappeared. On cooling, the slightly colored solution was washed with sodium bicarbonate, water, and dried with sodium sulfate. After the distillation of the toluene, 0.7 g of an oil ($n_D^{23.5}$ 1.5140) was obtained; it was hydrogenated with platinum dioxide in alcohol, 52 ml of hydrogen being absorbed in this process. After the distillation of the alcohol, 0.07 g of an oil ($n_D^{18.5}$ 1.5110) was obtained. A benzene solution of the oil was poured into a glass tube filled with a layer of aluminum oxide (height 15 cm) which had been moistened with petroleum ether. The washing of the substance was carried out with benzene, chloroform and methanol successively. As a result, the following fractions were obtained: 1st, a liquid oil n_D^{19} 1.5040, 200 mg (from benzene); 2nd, a liquid oil, n_D^{21} 1.5030, 50 mg (from benzene); 3rd, a thick oil, n_D^{21} 1.5160, 50 mg (from chloroform), 4th, crystals of the original substance, 250 mg (from methanol).

From 100 mg of the first fraction a semicarbazone with a melting point of 195-196° was obtained (from aqueous alcohol). A mixed sample with the semicarbazone of cis-decalone (XVII), obtained in experiment (a) melted at 196-197°.

From 100 ml of the first fraction was obtained a mixture of 2,4-dinitrophenylhydrazones with a melting point of 135-139°. After several crystallizations from alcohol, the 2,4-dinitrophenylhydrazone of cis-decalone (XVII) was isolated in the form of an egg-yellow powder with a melting point of 144-145° (preliminary softening beginning at 138°).

Found %: N 15.30, 15.34. $C_{19}H_{26}O_4N_4$. Calculated %: N 14.96.

* Experiment (a) was conducted by S. N. Ananchenko.

From 50 mg of the second fraction was obtained a mixture of 2,4-dinitrophenylhydrazones with a melting point of approximately 140°. After 2 recrystallizations from alcohol, we obtained a second 2,4-dinitrophenylhydrazone of cis-decalone (XVII) with a melting point of 148-149°, in the form of shining orange plates.

Found %: N 15.46, 15.58. $C_{19}H_{26}O_4N_4$. Calculated %: N 14.96.

A mixed sample with the above-described 2,4-dinitrophenylhydrazone obtained from the first fraction (m.p. 144-145°), melted at 139-142° with preliminary softening.

c) 0.72 g of hydroxydecalone (VI) with a melting point of 105-106° in 20 ml of anhydrous xylene was dehydrated in the presence of 25 mg of p-toluenesulfonic acid, by the method described in the preceding experiment. The separation of a considerable amount of water was observed in the first ten minutes. Boiling was carried out for a total of one hour and ten minutes. After treatment, 0.6 g of an oil (n_D^{24} 1.5141) was obtained; it was hydrogenated in an alcoholic solution in the presence of platinum dioxide, whereupon 27 ml of hydrogen was absorbed, and after the addition of a fresh portion of the catalyst, 23 ml more of hydrogen was absorbed. The solution was filtered, the alcohol was distilled off, and the oil which remained (n_D^{25} 1.5045) was subjected to chromatography on aluminum oxide. The following fractions were obtained: the first – an oil, n_D^{21} 1.5059, 240 mg (from benzene); the second – an oil, n_D^{20} 1.5040, 100 mg (from benzene); the third – crystals, 130 mg (from chloroform); the fourth – crystals, 120 mg (from methanol).

From the first and second fractions was obtained the same semicarbazone of cis-decalone (XVII) with a melting point of 195-196° (from aqueous alcohol). A mixed sample with the semicarbazone from experiment (b) did not give a depression. The mixture of 2,4-dinitrophenylhydrazones which was obtained from 150 mg of the first fraction, melted at 120-130° (after two crystallizations from alcohol). The mixture of yellow crystals which was obtained as a result of twice-repeated chromatographic analysis, melted at 136-144°.

From the mother liquor, shining orange crystals with a melting point of 140-141° were isolated; after crystallization from alcohol, they melted at 148-149°. A mixed sample with the orange 2,4-dinitrophenylhydrazone of cis-decalone (XVII) from experiment (b) (m.p. 148-149°) did not give a depression. The fourth fraction proved to be the original alcohol (VI) (mixture test).

Trans-9-methyl-1-ethyl-6-ketodecahydronaphthalene (XVIII). 0.7 g of ketone alcohol (V), with a melting point of 104-105°, in 25 ml of anhydrous xylene was dehydrated with 22 mg of p-toluenesulfonic acid in the presence of pyrogallol, for one hour. After the ordinary treatment, 600 mg of an oil (n_D^{23} 1.5180) was obtained; on the hydrogenation of this oil, in the presence of platinum dioxide, in an alcohol solution, 42 ml of hydrogen was absorbed. The 550 mg of the oil which was obtained was subjected to chromatographic analysis over aluminum oxide. The following fractions were isolated: the first – a liquid, n_D^{21} 1.5190, 200 mg (from benzene); the second – a liquid, n_D^{21} 1.5190, 50 mg (from benzene); the third – a thick oil, about 170 mg (from methanol).

The first and second fractions were combined and again hydrogenated with platinum dioxide, whereupon, 20 ml of hydrogen was absorbed. After chromatographic analysis the following fractions were isolated: the first fraction – a liquid, n_D^{19} 1.5090, 150 mg (from benzene); the second fraction – a liquid, n_D^{21} 1.5050, 50 mg (from benzene).

From 80 mg of the first fraction was obtained the semicarbazone of trans-decalone (XVIII) with a melting point of 200-201° (from aqueous alcohol); the second recrystallization did not change the melting point.

Found %: N 16.10, 15.92. $C_{14}H_{25}ON_3$. Calculated %: N 16.72.

A mixed sample with the semicarbazone of cis-decalone (XVII) melted at 193-194°. From the second fraction was obtained the 2,4-dinitrophenylhydrazone of trans-decalone (XVIII) in the form of crystals, which were orange in color and melted at 156-157° (from alcohol). $\lambda_{max.}$ (in isooctane) 347 mμ.

Found %: N 14.97, 15.08. $C_{19}H_{26}N_4O_4$. Calculated %: N 14.96.

A mixed sample with the 2,4-dinitrophenylhydrazone of ketone (XVII) (m.p. 148-149°) melted at 138-144°, with preliminary softening at 130°.

From 60 mg of the first fraction was also obtained a mixture of 2,4-dinitrophenylhydrazones with a melting point of 140-142°. After three crystallizations from alcohol, the above-described 2,4-dinitrophenylhydrazone with a melting point of 156-157° was obtained. From the mother liquor, we succeeded in sorting out by mechanical means, a small amount of the crystals of a yellow powder, with a melting point of 125-126°.

Trans-9-methyl-1-vinyl-1-hydroxy-6-ketodecahydronaphthalene (IX). In a three-necked flask, equipped with a mercury seal, a mechanical stirrer, and alkaline tube (for protection against moisture), and cooled with a mixture of dry ice and acetone, was distilled about 180 ml of liquid ammonia. Then 0.5 g of finely ground lithium was added with strong stirring, and a solution of 3 g of the vinyl alcohol (III) in 100 ml of anhydrous ether was immediately added. The stirring was continued for 2 hours at a temperature of the bath of −50°, after which ferric nitrate crystals were added $Fe(NO_3)_3 \cdot xH_2O$, and the stirring was continued for about 20 minutes more, until the full disappearance of the blue coloration of the solution. The reaction mixture was decanted into a solution of 9 g of ammonium chloride in 90 ml of water, and the product was worked from this point on as in the acetylenic synthesis. From the ether extract was obtained 1.9 g of the vinyl alcohol (IX) with a melting point of 93-94°. In addition, 0.1 g of this alcohol was isolated from the chloroform extract. After three crystallizations from ether, the vinyl alcohol (IX) melted at 97-97.5°.

Found %: C 75.29, 75.12; H 9.59, 9.70. $C_{13}H_{20}O_2$. Calculated %: C 74.96; H 9.68.

The 2,4-dinitrophenylhydrazone of the vinyl ketone alcohol (IX) consists of gold needles with a melting point of 180-181°.

Found %: N 13.93, 13.91. $C_{19}H_{24}O_5N_4$. Calculated %: N 14.43.

Trans-1-ethinyl-9-methyl-1-hydroxy-6-decalone (VIII). In a three-necked round-bottomed flask, equipped with a mercury seal, a mechanical stirrer, an alkaline tube (for protection from moisture) and cooled with a mixture of dry ice and acetone, was distilled about 125 ml of liquid ammonia. Then, 2 g of the finely ground acetylenic alcohol (II) and 40 ml of anhydrous ether were introduced with stirring, after which 0.22 g of finely ground lithium was added. When the full decolorization of the reaction mixture had taken place, 2 g NH_4Cl (an excess) was added, and after mixing for 2 hours, the product was allowed to stand overnight. The next day, 20 ml of water was added, and the ordinary treatment was carried out. From the ether extract was obtained 1.03 g of the crystals of the acetylenic alcohol (VIII) with a melting point of 150.5-152°. After two crystallizations from benzene mixed with petroleum ether, the acetylenic alcohol (VIII) melted at 158.5-159.5°. The substance gives an acetylene test with an ammoniacal solution of silver oxide.

Found %: C 75.35, 75.23; H 8.51, 8.60. $C_{13}H_{18}O_2$. Calculated %: C 75.69; H 8.80.

A mixed sample with the acetylenic alcohol (XV) of the cis-series (m.p. 158°) melted at 132-133°.

The 2,4-dinitrophenylhydrazone of the acetylenic alcohol consists of gold crystals with a melting point of 199.5-200.5°.

Found %: C 59.02, 58.77; H 6.00, 5.85. $C_{19}H_{22}O_5N_4$. Calculated %: C 59.05; H 5.75.

Trans-9-methyl-1-ethyl-1-hydroxy-6-ketodecahydronaphthalene (V). a) 0.2 g of the vinyl ketone alcohol (IX) with a melting point of 94-95°, was hydrogenated in 7 ml of alcohol, in the presence of platinum dioxide. 26 ml of hydrogen was quickly absorbed (20°, 745 mm) (1 mole), and hydrogenation slowed down very much. A product with a melting point of 101-102° was obtained; after three crystallizations from ether, the product melted at 105-105.5°. A mixed sample with the above-described trans-hydroxydecalone (VI) melted at 81-84°.

b) 0.11 g of the acetylenic ketone alcohol (VIII) with a melting point of 155-156°, was hydrogenated exhaustively in an alcohol solution, in the presence of a Pd catalyst. After filtration and distillation of the solvent, crystals with a melting point of 104-105° were obtained (from ether). A mixed sample with hydroxydecalone (V) did not give a depression.

Trans-9-methyl-1,6-diketodecahydronaphthalene (XXI). a) Into a flask, containing 250 ml of liquid ammonia, 370 mg of lithium and a solution of 2 g of diketooctalene (I) in 45 ml of anhydrous ether were gradually introduced, with stirring. After 1.5 hours, the reaction mixture was decanted into a solution of 10 g of ammonium chloride in 70 ml of water. The solution was extracted with ether and chloroform. The extract was neutralized with carbonic acid, washed with water until it gave a neutral reaction, and dried with magnesium sulfate. The 0.69 g of oil which was obtained from the ether extract was subjected to chromatographic analysis. From the benzene fraction was isolated about 150 mg of the crystals of trans-diketodecalin (XXI) with a melting point of 53.5-54.5° (from ether).

Found %: C 73.40, 73.26; H 8.95, 9.05. $C_{11}H_{16}O_2$. Calculated %: C 73.3; H 8.95.

A mixed sample with the cis-isomer (XXII) (m.p. 65-66°) [1] melted at 38-39.5°; with the original diketooctalene, however, (m.p. 49.5-50°) it melted at 33-36°.

The 2,4-dinitrophenylhydrazone of trans-9-methyldiketodecalin (XXI), after boiling in a mixture of dioxan and ethyl acetate, had a melting point of 241-242°. λ max. (in isooctane) 363 mμ.

Found %: N 20.67, 20.73. $C_{23}H_{24}O_8N_8$. Calculated %: N 20.73.

A mixed sample with the bis-2,4-dinitrophenylhydrazone of cis-decalindione (XXII) (m.p. 230.5-231.5°) melted at 221.5-222.5°.

The disemicarbazone of trans-decalindione (XXI) melted at 238-239° (after boiling in ethyl acetate).

b) 1.91 g of dry ammonium chloride, 2 g of diketooctalene (I) in 40 ml of ether, and 0.25 g of lithium were added to 150 ml of liquid ammonia, with stirring. After 2.5 hours 1 more g of ammonium chloride was added, and the mixture was allowed to stand over night. From the ether extract was obtained 0.86 g of a dark oil. By chromatography 0.2 g of an oil which became dark on standing was isolated from the benzene fraction. On the repetition of the chromatography, about 0.16 g of trans-9-methyldiketodecalin (XXI) with a melting point of 53-54° was obtained.

Trans-9-methyl-1-vinyl-1,6-dihydroxydecahydronaphthalene (X). 0.27 g of lithium was dissolved in 200 ml of liquid ammonia and a solution of 1.3 g of the vinyl alcohol (III) in 40 ml of anhydrous ether was added with stirring. The stirring was continued for one hour and 15 minutes at −50°. Then, 15 ml of anhydrous methanol and 0.18 g of lithium were added by drops; the solution gradually became colorless. The stirring was continued for one hour. The treatment was carried out as was described above. From the ether extract was obtained 0.9 g of an oil, which crystallized on standing and the addition of acetone. After crystallization from ether with benzene, trans-vinyldecalindiol (X) melted at 137-137.5° with preliminary softening.

Found %: C 74.40, 74.20; H 10.79, 10.80. $C_{13}H_{22}O_2$. Calculated %: C 74.20; H 10.54.

The hydrogenation of diol (X). 0.18 g of the diol (X) was hydrogenated with a Pd catalyst in a solution of alcohol and dioxan. About 9 ml of hydrogen was absorbed. After three crystallizations from benzene mixed with ether, a saturated diol which melted at 155-156° was obtained. A mixed sample with the above-described trans-diol (VII) did not give a depression.

Cis-9-methyl-1-ethyl-1,6-dihydroxydecahydronaphthalene (XI). 0.58 g of lithium was dissolved in 120 ml of liquid ammonia and a solution of 0.7 g of cis-ketone alcohol (VI) in ether was added. After 10 minutes, 8 ml of methanol was added over the course of 5 minutes, by drops, with stirring and with the temperature of the bath at −50°, whereupon decolorization of the solution began. Then, 1.5 ml more of methanol was added, and after an hour, 4 g of dry ammonium chloride was also added to the reaction mixture. After 40 minutes, the usual treatment of the solution was carried out. Cis-diol (XI), with a melting point of 118-119°, was obtained (from benzene and ether).

Found %: C 73.73, 73.55; H 11.43, 11.42. $C_{13}H_{24}O_2$. Calculated %: C 73.53; H 11.39.

Cis-9-methyl-1-ethyl-1,6-dihydroxydecahydronaphthalene (XIII). 0.5 g of lithium was dissolved in 200 ml of liquid ammonia, and after 10 minutes, a solution of 1.27 g of ketone alcohol (XII) (m.p. 126-127°) in 120 ml of anhydrous ether was added with stirring and cooling to −50°. After 15 minutes, 20 ml of alcohol was added over the course of half an hour, and then 0.7 g more of lithium was added. After decolorization of the reaction mixture, 10 g of ammonium chloride was added, and the stirring continued for 2 more hours. The next day, after the addition of water, 1.2 g of crystals of the diol (XIII) were precipitated; the crystals were slightly soluble in the ordinary solvents. After two crystallizations from a large quantity of alcohol, decalindiol (XIII) melted at 231-232°. The substance was partly sublimed in the capillary.

Found %: C 73.50, 73.39; H 11.52, 11.36. $C_{13}H_{24}O_2$. Calculated %: C 73.53; H 11.39.

Trans-9-methyl-1-vinyl-6-keto-Δ^1 octahydronaphthalene (XIX). 1.9 g of the vinyl alcohol (IX) (m.p. 93-94°), 1 g of finely ground potassium bisulfate, and 0.05 g of pyrogallol were heated in a vacuum (60 mm) for 40 minutes at a temperature of the bath of 140-145°; the separation of water was then observed. Upon cooling, the reaction mixture was extracted with ether. The residue which remained was dissolved in water, and the solution was also extracted with ether. Both extracts were neutralized with a solution of sodium bicarbonate, washed with water and dried with magnesium sulfate. After the distillation of the ether, the substance was distilled at 118.5-120° at 5 mm. 0.75 g of trans-vinyloctalone (XIX) was obtained in the form of a colorless liquid, which quickly began to crystallize. The substance melted before purification at 43-44.5°, and after crystallization from ether, at 46-47°. The diene has a pleasant odor, reminiscent of terpenes.

Found %: C 81.88, 82.03; H 9.57, 9.56. $C_{13}H_{18}O$. Calculated %: C 82.06; H 9.54.

In the distillation column a solid tar and a layer of oil were formed; the oil was decanted and also crystallized (about 0.15 g). There was 0.8 g of tar in the residue.

The semicarbazone of the diene (XIX) melted with decomposition at 200.5-201.5° (from methanol).

Found %: N 16.87, 16.97. $C_{14}H_{21}ON_3$. Calculated %: N 16.99.

SUMMARY

On the condensation of 9-methyl-1,6-diketo-Δ^5-octahydronaphthalene (I) with lithium acetylide in liquid ammonia, acetylenic alcohol (II) was obtained with a yield of 70%; on the partial hydrogenation of the acetylenic alcohol (II) with a Pd catalyst (1 molecule of hydrogen) vinyl alcohol (III) was formed. On the reduction of these alcohols with lithium in liquid ammonia, acetylenic alcohol (VIII) and vinyl alcohol (IX), which belong to the trans-decalin series, were obtained with high yields. The analogous reduction of diketooctalene (I) gives trans-9-methyl-1,6-diketodecalin (XXI), while the catalytic hydrogenation of diketone (I) leads to the formation of cis-9-methyl-1,6-diketodecalin (XXII). The catalytic addition of 2 molecules of hydrogen to acetylenic alcohol (II) gives 9-methyl-1-ethyl-6-keto-1-hydroxy-Δ^5-octahydronaphthalene (IV); the further catalytic hydrogenation of this compound leads to the formation of a mixture of cis- and trans-9-methyl-1-ethyl-6-keto-1-hydroxydecalenes (VI) and (V) in a ratio of 7:5.

The dehydration of vinyl alcohol (IX) with potassium bisulfate leads to the formation of trans-9-methyl-1-vinyl-6-keto-Δ^1-octahydronaphthalene (XIX), which easily enters into a diene condensation reaction.

On the condensation of acetylene with methoxyoctalone (XIV) and with diketooctalene (I) in liquid ammonia, acetylenic alcohols (XV) and (II) were formed, with different spatial distribution of the substituents at the first carbon atom.

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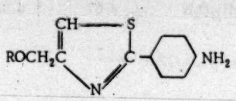
•See C. B. Translation, page 69, 799, 817, 827, 955, 969.

••See C. B. Translation, page 309.

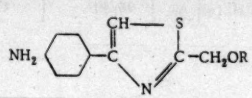
2-ALKOXYMETHYL- AND 2-ARYLOXYMETHYL-5-(p-AMINOPHENYL)-THIAZOLES

S. G. Fridman

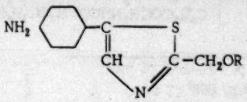
In our preceding papers [1, 2], we described the synthesis of substituted thiazoles of structures (A) and (B) (R = alkyl or aryl). In the present work we describe the preparation of the derivatives of thiazole (C), which differ from (B) only in the position of the p-aminophenyl radical:



(A)



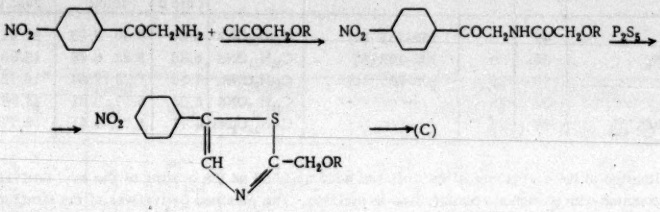
(B)



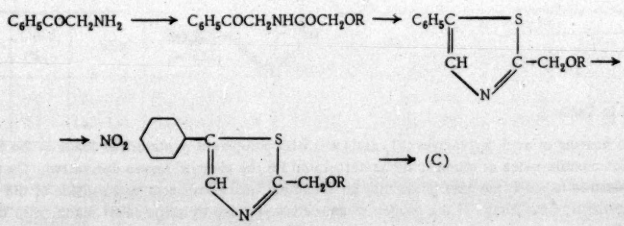
(C)

Compounds of type (C) were unknown up to the time this work was carried out. We proposed to accomplish their synthesis by two methods.

1. From p-nitro-ω-aminoacetophenone



2. From ω-aminoacetophenone



We were not able to follow the first method to its completion, since on the action of phosphorus pentasulfide on the nitrophenyl derivative, the reaction mixture would always burst into flames, and individual products of cyclization were not obtained. The second method turned out to be more favorable. All of the derivatives of thiazole which are described in this article were obtained by this method.

The condensation of ω-aminoacetophenone and p-nitro-ω-aminoacetophenone with the chloranhydrides of alkyl- and aryloxyacetic acids was carried out in chloroform in the presence of pyridine. The products which were obtained, their yields, melting points, boiling points, and the resultsof the analyses are given in Table 1.

The acyl derivatives, indicated in Table 1, are substances which crystallize well, with the exception of derivative compound No. (III).

TABLE 1

Compound No.	Formula	Yield (%)	Melting point	Empirical formula	Results of analysis for nitrogen (%)	
					calculated	found
I	$C_6H_5COCH_2NHCOCH_2OC_2H_5$	53	44°*	$C_{12}H_{15}O_3N$	6.33	6.30, 6.43
II	$p\text{-}NO_2C_6H_4COCH_2NHCOCH_2OC_2H_5$	–	100-101	$C_{12}H_{14}O_5N_2$	10.54	10.58, 10.36
III	$C_6H_5COCH_2NHCOCH_2OC_4H_9$	41	–**	$C_{14}H_{19}O_3N$	5.62	5.45, 5.51
IV	$C_6H_5COCH_2NHCOCH_2OC_6H_5$	60	98-98.8	$C_{16}H_{15}O_3N$	5.20	5.37, 5.39
V	$p\text{-}NO_2C_6H_4COCH_2NHCOCH_2OC_6H_5$	40	154-155	$C_{16}H_{17}O_5N_2$	8.91	8.94, 8.80
VI	$C_6H_5COCH_2NHCOCH_2OC_6H_4Br$ (p)	44	156-157	$C_{16}H_{14}O_3NBr$	4.02***	4.14, 4.21
VII	$C_6H_5COCH_2NHCOCH_2OC_6H_4Cl$ (p)	46	154-155	$C_{16}H_{14}O_3NCl$	4.61****	4.67, 4.79
VIII	$C_6H_5COCH_2NHCOCH_2OC_6H_4OCH_3$ (o)	40	96-97	$C_{17}H_{17}O_4N$	4.67	4.82, 4.90

* B.p. 191-192° (5 mm).

** B.p. 208° (3 mm).

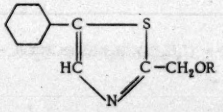
*** Bromine content (%): calculated 22.88, found 22.87, 22.76.

**** Chlorine content (%): calculated 11.68, found 11.80, 11.94.

TABLE 2

Compound No.	R	Yield (%)	M.p.	B.p. (pressure, mm)	Empirical formula	Results of analysis (%)			
						nitrogen		sulfur	
						calc'd	found	calc'd	found
IX	C_2H_5	49	–	153-155° (5)	$C_{12}H_{13}ONS$	6.39	6.40, 6.23	14.61	14.61, 14.60
X	$n\text{-}C_4H_9$	50	–	190-192 (8)	$C_{14}H_{17}ONS$	5.66	5.83, 5.68	12.95	13.00, 13.10
XI	H	70	90	205-208 (18)	$C_{10}H_9ONS$	7.33	7.30, 7.44	16.75	16.40, 16.47
XII	C_6H_5	50	65	–	$C_{16}H_{13}ONS$	5.24	5.37, 5.31	11.98	12.07, 12.04
XIII	$o\text{-}CH_3OC_6H_4$ . . .	48	90	–	$C_{17}H_{15}O_2NS$	4.71	4.71, 4.41	10.77	10.30, 10.17

The cyclization to the derivatives of thiazole was accomplished on the heating of the acyl derivatives of ω-aminoacetophenone with phosphorus pentasulfide in pyridine. The obtained derivatives of the structure:



are given in Table 2.

The heating of acyl derivatives (VI) and (VII) with phosphorus pentasulfide leads to the formation of products which contain twice as much sulfur as calculated for the phenylthiazole derivative. On the basis of analysis, it is possible to reach the conclusion that on the fusion with phosphorus pentasulfide of the indicated compounds the replacement of the atoms of the oxygen of the carbonyl group by sulfur takes place, with the formation of the compound

$$C_6H_5CSCH_2NHCSCH_2OC_6H_4X \quad (X = Cl, Br),$$

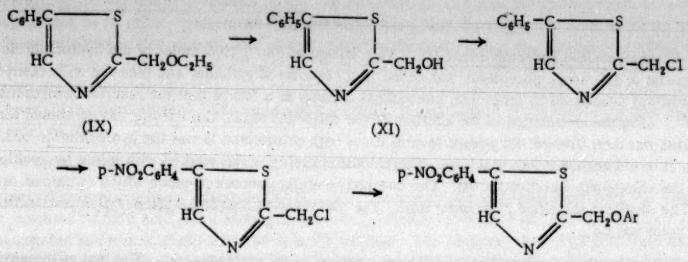
but cyclization does not take place.

On the nitration of 2-ethoxymethyl-5-phenylthiazole, 2-ethoxymethyl-5-(p-nitrophenyl)-thiazole was isolated (XVI, Table 3). The position of the nitro group was shown by the oxidation of the compound to p-nitrobenzoic acid.

On the nitration of 2-butoxymethyl-5-phenylthiazole, a liquid product was obtained; we did not succeed in isolating this product in the pure form. 2-n-Butoxymethyl-5-(p-nitrophenyl)-thiazole was identified in the form of

its hydrochloride and the benzoyl derivative of the corresponding amine – the product of its reduction.

On the nitration of the 2-aryloxy derivatives of thiazole (XII) and (XIII), one should expect the formation, in the first place, of the nitroaryloxy derivatives; it was, therefore, necessary to proceed in this case, by an indirect method. The alkoxymethyl group in substance (IX) was saponified to the oxymethyl group, and the latter was then converted into the chloromethyl group. The 2-chloromethyl-5-phenylthiazole was subjected to nitration, and then the active chlorine atom was replaced by an aryloxy group by the action of phenolates:



(IX) (XI)

2-Oxymethyl-5-phenylthiazole (XI) was isolated on the saponification of 2-ethoxymethyl-5-phenylthiazole with 75% sulfuric acid. It was converted into the chloromethyl derivative by the action of thionyl chloride.

The nitration of the chloromethyl derivative and the treatment of the product with phenolates was carried out analogously to the procedure we have described earlier [1].

TABLE 3

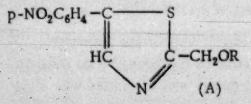
Compound No.	R	Yield (%)	M.p.	Empirical formula	Results of analysis (%)			
					nitrogen		sulfur	
					calculated	found	calculated	found
XVI	C_2H_5	51	65°	$C_{12}H_{12}O_3N_2S$	10.60	10.68, 10.80	12.12	11.92, 11.96
XVII	C_6H_5	50	153-154	$C_{16}H_{12}O_3N_2S$	8.94	9.12, 9.15	10.25	9.98, 10.05
XVIII	p-ClC_6H_4 . .	64	158	$C_{16}H_{11}O_3NSCl$	8.08	8.28, 8.30	9.23	9.39, 9.29

TABLE 4

Compound No.	R	Yield (%)	M.p.	Empirical formula	Results of analysis (%)			
					nitrogen		sulfur	
					calculated	found	calculated	found
XIX	C_6H_5	70	114-115°	$C_{16}H_{14}ON_2S$	9.92	9.93, 9.82	11.34	11.23, 11.40
XX	p-ClC_6H_4 . .	65	113-114	$C_{15}H_{19}ON_2SCl$	8.84	8.79, 8.64	10.11	10.18, 10.26

TABLE 5

R	Hydrochloride				Acyl derivative			
	m.p.	empirical formula	results of analysis for nitrogen (%)		m.p.	empirical formula	results of analysis for nitrogen (%)	
			calc'd	found			calc'd	found
C_2H_5	–	$C_{12}H_{17}O_2N_2SCl$	9.74	9.39, 9.49	129°	$C_{14}H_{16}O_2N_2S$	10.14	10.02, 10.21
C_6H_5	216-217°	$C_{16}H_{15}ON_2SCl$	8.75	8.90, 9.01	180	$C_{18}H_{16}O_2N_2S$	8.64	8.60, 8.51
p-ClC_6H_4	200-201	$C_{16}H_{14}ON_2SCl_2$	7.93	8.25, 8.26	214	$C_{18}H_{15}O_2N_2SCl$	7.81	7.90, 8.08
						Benzoyl derivative		
n-C_4H_9	185-186	$C_{14}H_{21}O_2N_2SCl$	8.84	8.64, 8.60	140	$C_{21}H_{22}O_2N_2S$	7.65	7.44, 7.37



(A)

In Table 3 are given the 5-(p-nitrophenyl)-thiazoles of structure (A).

Reduction to the corresponding amines was carried out in a water-alcohol medium with iron filings, in the presence of acetic acid. In the free state, only two amines were isolated. The amines obtained are given in Table 4. The remaining amines were identified in the form of their hydrochlorides, and their acyl derivatives, the characteristics of which are given in Table 5.

EXPERIMENTAL

ω-Ethoxyacetylaminoacetophenone (I). To a charge of 85.7 g (0.5 mole) of the hydrochloride of ω-aminoacetophenone in 400 ml of chloroform, was added 79 g (1 mole) of pyridine, and then the chloroanhydride of ethoxyacetic acid* was introduced by drops with mechanical stirring, at a rate so that the reaction temperature did not rise above 30°. After the completion of the addition of the chloroanhydride, the stirring was continued for 4 more hours. The residue was then filtered and washed several times with chloroform; it was the hydrochloride of ω-aminoacetophenone; it would not enter into reactions. The chloroform solution was washed with dilute hydrochloric acid, water, and the chloroform was distilled off. The ω-ethoxyacetylaminoacetophenone which remained, was vacuum distilled. The distillate solidified after some time. The yield was 58.5 g (53%); after crystallization from alcohol the melting point was 44°.

ω-Butoxyacetylaminoacetophenone (III) was prepared in an analogous way. The rest of the acyl derivatives (II, IV, V, VI, VII and VIII) were not distilled after the driving off of the chloroform, but were decanted with water. The oil which was precipitated in these cases, solidified after some time. The product was filtered, washed with dilute hydrochloric acid, water, and crystallized from alcohol.

2-Ethoxymethyl-5-phenylthiazole (IX). A well-ground mixture of 47.9 g of ω-ethoxyacetylaminoacetophenone and 48 g of phosphorus pentasulfide was drenched with 150 ml of dry pyridine, and the reaction mixture was boiled for 45 minutes. The hot solution was decanted with 500 ml of boiling water, and the oil which was precipitated, on cooling, was extracted with chloroform. The chloroform solution was filtered, washed twice with a 10% solution of sodium hydroxide and with water. After the distillation of the solvent, the residue was dissolved in concentrated hydrochloric acid, and the solution was filtered from the solid, insoluble admixtures. The filtrate was diluted with a large amount of water, the oil which was precipitated was extracted with ether, the ether solution was dried with roasted sodium sulfate, and the residue, after the ether was distilled off, was vacuum distilled. The yield was 23 g (49%); the boiling point was 153-155° at 5 mm.

2-n-Butoxymethyl-5-phenylthiazole (X) was prepared in an analogous way. The crystalline compounds (XII, XIII) were not distilled, but were purified by crystallization from alcohol.

2-Oxymethyl-5-phenylthiazole (XI). To 25 g of 2-ethoxymethyl- or 2-butoxymethyl-5-phenylthiazole was added 75 ml of 75% sulfuric acid, and the mixture was heated on an oil bath for 30 minutes at 140-145°. The solution which was formed, was decanted onto ice (300 g), neutralized with a 30% solution of sodium hydroxide, and the oil which precipitated was extracted several times with ether. After drying with sodium sulfate, the ether was distilled off, and the residue was vacuum distilled. The yield was 15.2 g (70%), the boiling point was 205-208° at 12 mm. The distillate solidified upon standing. The compound melted at 90°, after crystallization from dilute alcohol.

Attempts to saponify 2-phenoxymethyl-5-phenylthiazole to the 2-oxymethyl derivative under the same conditions with sulfuric acid led to the formation of a product which did not melt up to 300°. The analysis for nitrogen and sulfur corresponds to the product of the sulfonation of 2-phenoxymethyl-5-phenylthiazole.

Found %: N 3.69, 3.77; S 17.50, 17.28. $C_{16}H_{13}C_5NS_2$. Calculated %: N 3.84; S 17.59.

2-Chloromethyl-5-phenylthiazole (XIV). To a solution of 10 g of 2-oxymethyl-5-phenylthiazole in 75 ml of dry chloroform, a solution of 7 g of thionyl chloride in 15 ml of chloroform was added with stirring and mild heating over a water bath. The mixture boiled moderately during the process. After the completion of the addition of the thionyl chloride, the heating was stopped, and the stirring was continued for 2 more hours, whereupon a crystalline precipitate of the hydrochloride of 2-chloromethyl-5-phenylthiazole settled on the walls of the reaction vessel. It was filtered and washed with chloroform. The weight of the salt was 7.6 g; its melting point was 146°. The salt, on the addition of water was hydrolyzed and an oily product was isolated; the oily product was extracted with ether. The ether solution was washed with a solution of soda, and after drying with sodium sulfate, the ether was distilled off. The base which remained quickly solidified. On distillation in a vacuum, it decomposed; there-

* (61.3 g, 0.5 mole).

fore, the base was again converted into the hydrochloride by the action of an ether solution of hydrogen chloride; its melting point was 146°.

Found %: Cl 24.63. $C_{10}H_9NSCl_2$. Calculated %: Cl 24.79.

The hydrochloride of 2-chloromethyl-5-phenylthiazole, like other chloromethyl derivatives of the phenylthiazoles, causes serious irritation of the skin.

2-Chloromethyl-5-(p-nitrophenyl)-thiazole (XV). To a solution of 11.6 g of the hydrochloride of 2-chloromethyl-5-phenylthiazole in 75 ml of concentrated sulfuric acid, was added, by drops, a mixture of 20 ml of nitric acid (d 1.5) in 20 ml of concentrated sulfuric acid at 0-2°, with mechanical stirring; the mixture was added over the course of 30 minutes. On the completion of the addition of the nitrating mixture, the stirring was continued for 30 minutes more, then the mixture was decanted onto ice (300 g). The light yellow precipitate was filtered, washed with water and crystallized from alcohol. The yield was 9 g (75%). It crystallized in the form of yellow needles with a melting point of 103°.

Found %: N 10.80, 10.92; Cl 13.78, 13.84. $C_{10}H_7O_2N_2SCl$. Calculated %: N 11.00; Cl 13.94.

2-Ethoxymethyl-5-(p-nitrophenyl)-thiazole (XVI). 5 g of 2-ethoxymethyl-5-phenylthiazole was dissolved in 10 ml of concentrated sulfuric acid, with cooling in a freezing mixture; a mixture of 7 ml of nitric acid (d 1.5) and 7 ml of concentrated sulfuric acid was then added to the solution. The product was crystallized from alcohol. The position of the nitro group was determined by oxidation with potassium bichromate in sulfuric acid [1]. The product of oxidation had a melting point of 238°, and did not give a depression with p-nitrobenzoic acid.

In the product of the nitration of 2-chloromethyl-5-phenylthiazole, the position of the nitro-group was not specifically determined, since only one nitro compound was obtained, and it, no doubt, should be considered a p-nitro derivative.

2-n-Butoxymethyl-5-(p-nitrophenyl)-thiazole was obtained analogously to the preceding compound (XVI). It is a liquid that does not distil without decomposition; we did not succeed in obtaining it in the pure form.

2-Phenoxymethyl-5-(p-nitrophenyl)-thiazole (XVII). To a solution of 3.8 g (0.015 mole) of 2-chloromethyl-5-(p-nitrophenyl)-thiazole in 75 ml of dry acetone was added 1.8 g (0.02 mole) of phenol and 2.7 g (0.02 mole) of anhydrous potash. The mixture was boiled for 20 hours over a water bath, the acetone was distilled off, the residue was suspended in water, filtered, washed with a 10% solution of sodium hydroxide, water, and crystallized from glacial acetic acid. The yield was 2.3 g (50%); the melting point was 153-154°. Compound (XVIII) was prepared in an analogous way. The reduction of the nitro-derivative was carried out with iron filings in a water-alcohol medium, with the addition of acetic acid. The amines were identified either in the form of the bases (Table 4), or in the form of the hydrochlorides and acyl derivatives (Table 5).

SUMMARY

From ω-alkoxy- and aryloxyacetylaminoacetophenones were obtained: 2-ethoxymethyl-, 2-n-butoxymethyl-, 2-phenoxymethyl-, 2-o-methoxyphenoxymethyl-, 2-oxymethyl-, and 2-chloromethyl-5-phenyl-thiazole. By the nitration of 2-ethoxymethyl- and 2-chloromethyl-5-phenylthiazoles were obtained the corresponding p-nitrophenyl derivatives, and from them, four amines: 2-ethoxymethyl-, 2-n-butoxymethyl-, 2-phenoxymethyl-, and 2-p-chlorophenoxymethyl-5-p-aminophenylthiazole.

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* See Consultants Bureau Translation, page 651.

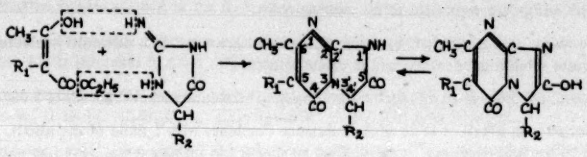
STUDIES IN THE FIELD OF PYRIMIDINOIMIDAZOLONES

II. THE SYNTHESIS OF PYRIMIDINOIMIDAZOLONES ON THE BASIS OF THE LACTAM OF α-GUANIDOPROPIONIC ACID

M. A. Prokofyev and Yu. P. Shvachkin

One of the possible methods of the synthesis of pyrimidinoimidazolones [1] is the condensation of the lactams of guanido acids with compounds of the type of acetoacetic and malonic esters. Earlier [2], the preparation of similar compounds on the basis of the lactam of guanidoacetic acid was described. In the present work, we continued the preparation of pyrimidinoimidazolones, starting from the lactam of guanidoacetic acid, and also brought into the indicated reaction the condensation of the lactam of α-guanidopropionic acid.

Acetoacetic ester and its derivatives were condensed with the lactams of α-guanidopropionic and guanidoacetic acids according to the scheme:



I. $R_1 = H$; $R_2 = CH_3$. II. $R_1 = C_2H_5$; $R_2 = CH_3$. III. $R_1 = n\text{-}C_4H_9$; $R_2 = CH_3$. IV. $R_1 = n\text{-}C_4H_9$; $R_2 = H$.

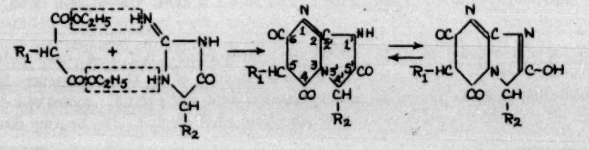
The condensation reaction was carried out in an alcohol medium in the presence of sodium alcoholate.

The reaction products were separated on the basis of the fact that, on the acidification of the reaction mixture to a pH of 1-4 (depending on the character of the compounds which are to be separated) the pyrimidinoimidazolones which are formed precipitate out, while the unreacted lactams and other substances remain in solution.

The obtained compounds are colorless crystalline substances with high melting points. They are insoluble in ether, chloroform, and acetone, difficultly soluble in cold water and the lower alcohols; they are insoluble in acids, but are easily dissolved in dilute bases.

Upon interaction with alkalis, the obtained pyrimidinoimidazolones quantitatively combine with one mole of the alkali per mole of the substance, that is, they act like monobasic acids. This is explained, evidently, by the presence in the obtained compounds of an acid hydrogen atom, which is formed due to lactim-lactam tautomerism.

The malonic ester and its derivatives enter into analogous condensation reactions with the lactams of guanidoacetic and α-guanidopropionic acids:



V. $R_1 = H$; $R_2 = CH_3$. VI. $R_1 = C_2H_5$; $R_2 = CH_3$. VII. $R_1 = n\text{-}C_4H_9$; $R_2 = CH_3$. VIII. $R_1 = C_6H_5$; $R_2 = H$.

Compounds of this type are also colorless crystalline substances with high melting points. But, unlike the pyrimidinoimidazolones of the first type (from acetoacetic ester and its derivatives) they have higher acidic properties, and on interaction with alkalis they combine with more than one mole of the alkali per mole of the substance. This is explained, probably, by the fact that in compounds of this type, in addition to the acid hydrogen atom, which is found in the imidazolone ring, and is characteristic, evidently, for all pyrimidinoimidazolones-5', there is the possibility of acidic groups arising in the pyrimidino ring on account of keto-enol tautomerism.

EXPERIMENTAL

1. The Preparation of 4-oxo-6-methyl-dihydropyrimidino-2,3:2',3'-4'– methyldihydroimidazolone-5' (I). In a three-necked flask, equipped with a mechanical stirrer, a dropping funnel and a reflux condenser, protected with a calcium chloride tube, was prepared an alcohol solution of sodium ethylate from 50 ml of anhydrous ethyl alcohol and 1.38 g (0.06 g-atom) of metallic sodium. To the solution was added with stirring, 1.5 g (0.01 mole) of the hydrochloride of the lactam of α-guanidopropionic acid [3] and the stirring was continued at room temperature for 10 minutes (in order to separate the free lactam of α-guanidopropionic acid from its hydrochloride).* Then the mixture was heated on a glycerin bath until boiling, and 6.7 g (0.05 mole) of acetoacetic ester was added to it by drops, after which the boiling of the mixture on the glycerin bath (at a temperature of 110-115°) was continued for 5 hours. Then the mixture was evaporated in a vacuum until dry, and the residue was treated with a quantity of 5% hydrochloric acid such that the solution which was formed had a pH of 4.

The substance which precipitated out was filtered, washed with ether, crystallized from 86 parts of boiling water and dried at 135°. 0.94 g (52.5%) was obtained. From water the substance crystallizes in the form of shining plates with a melting point of 282° (decomposition). A mixed sample of the substance with the compound prepared by other means [1] did not give a depression of the melting point.

The substance was insoluble in ether, benzene, chloroform, acetone. It is difficultly soluble in cold water and alcohol. It is quite soluble in hot water and in dilute alkalis.

Found %: C 53.67; H 5.40; N 23.40 (Kjeldahl). $C_8H_9O_2N_3$. Calculated %: C 53.63; H 5.03; N 23.46.

On interaction with alkali, a mole of the substance combines with 1 mole of the alkali. The determination was carried out in the following way: to a weighed portion of the substance was added an excess (compared with the calculated amount) of a 0.1 N solution of potassium hydroxide, and in the obtained solution the excess alkali was back-titrated with a 0.1 N solution of sulfuric acid with a phenolphthalein indicator.

0.0593 g sub.: 3.17 ml 0.1 N KOH. Calculated: 3.21 ml 0.1 N KOH.

2. The preparation of 4-oxo-6-methyl-5–ethyldihydropyrimidino-2,3:2',3'-4'–methyldihydroimidazolone-5' (II). The compound was prepared analogously to the preceding compound, from 1.5 g (0.01 mole) of the hydrochloride of the lactam of α-guanidopropionic acid, 7.9 g (0.05 mole) of ethylacetoacetic ester [4] and 1.38 g (0.06 g-atom) of metallic sodium in 50 ml of anhydrous ethyl alcohol. Acidification with 5% hydrochloric acid was carried out until a pH of 1 was reached. The substance which was separated was filtered, washed with ether and cold water, and crystallized from 38 parts of boiling 96% ethyl alcohol. 1.05 g (50.7%) was obtained.

From alcohol the substance crystallized in the form of thin rods, collected in small clusters. Melting point 263°. The substance is quite soluble in hot alcohol, readily in dilute alkalis, difficultly soluble in cold alcohol and in hot water, and is insoluble in cold water, ether, benzene and acetone.

6.290 mg sub.: 13.111 mg CO_2; 3.595 mg H_2O. 0.0717 g sub.: 10.32 ml 0.1 N H_2SO_4. Found %: C 58.20; H 6.54; N 20.15. $C_{10}H_{13}O_2N_3$. Calculated %: C 57.96; H 6.32; N 20.28.

On interaction with alkali, 1 mole of the substance combines with one mole of the alkali.

0.0500 g sub.: 2.31 ml 0.1 N KOH. 0.0567 g sub.: 2.64 ml 0.1 N KOH. Calculated: 2.50, 2.67 ml 0.1 N KOH.

3. The preparation of 4-oxo-6-methyl-5-n-butyldihydropyrimidino-2,3:2',3'-4'–methyldihydroimidazolone-5' (III). The substance was prepared analogously to the preparation of the above substance, from 1.5 g (0.01 mole) of the hydrochloride of the lactam of α-guanidopropionic acid, 9.3 g (0.05 mole) of n-butylacetoacetic ester [5] and 1.38 g (0.06 g-atom) of sodium in 50 ml of anhydrous ethyl alcohol. The heating continued for 5

* As was shown experimentally, the sodium chloride which is formed as a by-product in this process does not hinder the further progress of the condensation reaction.

hours. The dry residue, obtained after the evaporation of the mixture in a vacuum, was acidified with 5% hydrochloric acid until pH 1; thereupon, the substance was isolated in the form of an oil which crystallized upon standing. The crystalline product was filtered, washed with ether and recrystallized from 24 parts of boiling ethyl alcohol. 0.77 g (32.8%) of a colorless substance which had a slight luster and melted at 229° was obtained.

From ethyl alcohol the compound was crystallized in the form of thin rods, from n-butyl alcohol – in the form of needles, collected in fan-shaped clusters.

The substance is quite soluble in ethyl and n-butyl alcohols on heating, and is very soluble in dilute alkalis, is difficultly soluble in hot water, cold ethyl alcohol, and is insoluble in ether and in cold water.

0.0867 g sub.: 11.04 ml 0.1 N H_2SO_4. 0.0773 g sub.: 9.85 ml 0.1 N H_2SO_4. Found %: N 17.83, 17.84. $C_{12}H_{17}O_2N_3$. Calculated %: N 17.86.

On the interaction of the substance with alkali, one mole of the substance combines with 1 mole of the alkali.

0.0562 g sub.: 2.35 ml 0.1 N KOH. 0.0475 g sub.: 1.94 ml 0.1 N KOH. Calculated: 2.32, 1.96 ml 0.1 N KOH.

4. The preparation of 4-oxo-6-methyl-5- n–butyldihydropyrimidino-2,3:2',3'-dihydroimidazolone-5' (IV). This substance was prepared analogously to the preparation of the preceding compounds, from 1 g (0.01 mole) of the lactam of guanidoacetic acid [6] and 9.3 g (0.05 mole) of n-butylacetoacetic ester in a medium of anhydrous alcohol in the presence of sodium ethylate. After acidification to pH 1, the substance was separated in the form of a yellow oil, which spontaneously crystallized upon standing. The crystalline product was filtered, carefully washed with ether and recrystallized from 45 parts of 96% ethyl alcohol. 0.62 g (28%) of the substance was obtained. The compound was crystallized from alcohol in the form of short rods. Their melting point was 252°.

The substance is quite soluble in hot ethyl alcohol, hot n-butyl alcohol, and dilute alkalis; it is difficultly soluble in hot water, and is insoluble in ether and in cold water.

6.210 mg sub.: 13.583 mg CO_2; 3.844 mg H_2O. 2.228 mg sub.: 0.375 ml N_2 (23°, 749 mm). Found %: C 59.69; H 6.92; N 19.14. $C_{11}H_{15}O_2N_3$. Calculated %: C 59.71; H 6.83; N 18.99.

On interaction with alkali, one mole of the substance combines with one mole of the alkali.

0.0586 g sub.: 2.51 ml 0.1 N KOH. 0.0438 g sub.: 1.96 ml 0.1 N KOH. Calculated: 2.67, 1.96 ml 0.1 N KOH.

5. The preparation of 4,6 –dioxotetrahydropyrimidino-2,3:2',3',4' –methyldihydroimidazolone-5' (V). The compound was prepared analogously to the preparation of the preceding compounds from 1.5 g (0.01 mole) of the hydrochloride of the lactam of α-guanidopropionic acid, 8 g (0.05 mole) of malonic ester, and 1.38 g (0.06 g-atom) of sodium in 50 ml of anhydrous ethyl alcohol. The mixture was boiled for 5 hours, then it was evaporated in a vacuum until dry, and treated with 5% hydrochloric acid. The product began to precipitate at pH 6. Acidification was carried out until pH 3. One hour later, the substance which had been separated was filtered, washed with ether, decolorized with animal charcoal, and recrystallized from 28 parts of boiling water. 1.05 g (58%) of the substance was obtained. The substance crystallized from water in the form of parallelograms with a melting point of 225°.

8.496 mg sub.: 14.446 mg CO_2; 3.044 mg H_2O. 0.0766 g sub.: 12.68 ml 0.1 N H_2SO_4. Found %: C 46.30; H 4.00; N 23.17. $C_7H_7O_3N_3$. Calculated %: C 46.41; H 3.89; N 23.20.

On interaction with alkali, one mole of the substance combines with about 1.5 moles of the alkali.

0.0621 g sub.: 5.16 ml 0.1 N KOH. 0.0481 g sub.: 4.15 ml 0.1 N KOH. Calculated for reaction with 1 mole of alkali: 3.43, 2.65 ml 0.1 N KOH.

6. The preparation of 4,6-dioxo-5 –ethyltetrahydropyrimidino-2,3:2',3'-4'– methyldihydroimidazolone-5' (VI). The substance was prepared analogously to the preceding compounds from 1.5 g (0.01 mole) of the hydrochloride of the lactam of α-guanidopropionic acid, 7.5 g (0.04 mole) of ethylmalonic ester [6], and 1.15 g (0.05 g-atom) of sodium in 50 ml of anhydrous ethyl alcohol. The acidification was carried out with 5% hydrochloric acid until a pH of 2 was reached. The substance which was separated was filtered, washed with ether, and recrystallized from 75 parts of boiling water. 1.25 g (59.8%) of a colorless powder was obtained, it melted with decomposition at 290-291°.

The substance is comparatively soluble in hot water and in hot ethanol, quite soluble in dilute alkalis, difficultly soluble in cold ethanol, and insoluble in cold water and in ether.

7.126 mg sub.: 13.562 mg CO_2; 3.571 mg H_2O. 0.0892 g sub.: 12.72 ml 0.1 N H_2SO_4. Found %: C 51.94; H 5.60; N 19.96. $C_9H_{11}O_3N_3$. Calculated %: C 51.67; H 5.30; N 20.09.

On interaction with alkali, one mole of the substance combines with approximately 1.2 moles of the alkali.

0.0622 g sub.: 3.52 ml 0.1 N KOH. 0.0534 g sub.: 3.17 ml 0.1 N KOH. Calculated for reaction with 1 mole of alkali: 2.80, 2.55 ml 0.1 N KOH.

7. The preparation of 4,6-dioxo-5-n-butyltetrahydropyrimidino-2,3:2',3'-4'-methyldihydroimidazolone-5' (VII). The substance was prepared analogously to the preceding substances from 1.5 g (0.01 mole) of the hydrochloride of the lactam of α-guanidopropionic acid, and 4.32 g (0.02 mole) of n-butylmalonic ester [8] in a medium of anhydrous ethyl alcohol in the presence of sodium ethylate. After 5 hours of boiling, the mixture was evaporated in a vacuum, and the residue was acidified with 5% hydrochloric acid to pH 2. The substance precipitated in the form of large drops of a yellow oil, which quickly crystallized upon standing. The crystalline product was filtered, carefully washed with ether, worked with water which had been heated to 50°, and dried at 130°. 1.67 g (70.5%) of a cream-colored powder was obtained; it melted at 228°.

The substance was soluble upon heating in methyl, ethyl, and n-butyl alcohol, soluble in dioxan, glacial acetic acid, and formic acid, very soluble in dilute alkalis, difficultly soluble in hot water and in boiling chloroform, insoluble in ether, benzene, and in cold water. Upon being heated above 60°, the substance is easily converted into an oil.

0.0882 g sub.: 10.96 ml 0.1 N H_2SO_4. 0.0803 g sub.: 9.95 ml 0.1 N H_2SO_4. Found %: N 17.40, 17.35. $C_{11}H_{15}O_3N_3$. Calculated %: N 17.71.

On interaction with alkali, one mole of the substance combines with approximately 1.2 moles of the alkali.

0.0620 g sub.: 3.20 ml 0.1 N KOH. 0.0485 g sub.: 2.49 ml 0.1 N KOH. Calculated for reaction with 1 mole of alkali: 2.60, 2.03 ml 0.1 N KOH.

8. The preparation of 4,6-dioxo-5-phenyltetrahydropyrimidino-2,3:2',3'-dihydroimidazolone-5'(VIII). The substance was prepared analogously to the preceding substances, from 1 g (0.01 mole) of the lactam of guanidoacetic acid, 7.08 g (0.03 mole) of phenylmalonic ester [9], and 0.92 g (0.04 g-atom) of sodium in 50 ml of anhydrous ethyl alcohol. After boiling for 5 hours, the mixture was evaporated in a vacuum and acidified with 5% hydrochloric acid to pH 1. The substance which was precipitated was filtered, washed with ether, decolorized with bone black, and recrystallized from 450 parts of boiling water. 1.31 g (53.9%) of the substance was obtained. It crystallized from water in the form of short needles with a melting point of 315° (decomposition).

The substance is very soluble in dilute alkalis, difficultly soluble in boiling water, hot alcohol and dioxan, and insoluble in benzene, acetone, ether, and cold water.

0.0903 g sub.: 11.12 ml 0.1 N H_2SO_4. 0.0761 g sub.: 9.44 ml 0.1 N H_2SO_4. Found %: N 17.24, 17.37. $C_{12}H_9O_3N_3$. Calculated %: N 17.28.

On interaction with alkali, one mole of the substance combines with about 1.4 moles of the alkali.

0.0605 g sub.: 3.62 ml 0.1 N KOH. 0.0483 g sub.: 2.83 ml 0.1 N KOH. Calculated for reaction with 1 mole of alkali: 2.48, 1.98 ml 0.1 N KOH.

SUMMARY

1. It has been shown that the lactam of α-guanidopropionic acid may enter into a condensation reaction with the derivatives of acetoacetic and malonic esters, which leads to the formation of the corresponding pyrimidino-2,3:2';3'-imidazolones-5'.

2. The following pyrimidinoimidazolones, which have not been described previously in the literature, have been synthesized: 4-oxo-6-methyl-5-ethyldihydropyrimidino-2,3:2',3'-4'-methyldihydroimidazolone-5'; 4-oxo-6-methyl-5-n-butyldihydropyrimidino-2,3:2',3'-4'-methyldihydroimidazolone-5'; 4-oxo-6-methyl-5-n-butyldihydropyrimidino-2,3:2',3'-dihydroimidazolone-5'; 4,6-dioxotetrahydropyrimidino-2,3:2',3'-4'-methyldihydroimidazolone-5'; 4,6-dioxo-5-ethyltetrahydropyrimidino-2,3:2',3'-4'-methyldihydroimidazolone-5'; 4,6-dioxo-5-n-butyltetrahydropyrimidino-2,3:2',3'-4'-methyldihydroimidazolone-5'; 4,6-dioxo-5-phenyl-tetrahydropyrimidino-2,3:2',3'-dihydroimidazolone-5'. 4-oxo-6-methyldihydropyrimidino-2,3:2',3'-4'-methyldihydroimidazolone-5' was prepared by a new method.

3. It has been established that the obtained pyrimidinoimidazolones have acid properties, which is, evidently, explained by the presence in these compounds of acid groups, which are formed as a result of tautomeric transformations in the imidazolone and pyrimidino rings.

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SYNTHESES ON THE BASIS OF ANABASINE

XI. THE HYDROLYSIS OF N-(β-PROPIONITRILE)-ANABASINE

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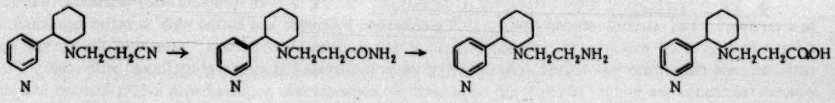
In our preceding communication [1], we described the reaction of the addition of ethyl cyanide to anabasine. Later, we studied the conditions of the hydrolysis of N-(β-propionitrile)-anabasine (I).

On the hydrolysis of N-(β-propionitrile)-anabasine with cold concentrated sulfuric acid, by the method described previously by a number of authors [2], N-(β-propionamide)-anabasine (II) was obtained with a yield of 34.4%. On the action of bromine and a solution of potassium hydroxide [3] on compound (II), N-(β-aminoethyl)-anabasine (III) was formed (yield 46.0%). N-(β-Aminoethyl)-anabasine is an oil which becomes dark quickly, and crystallizes with difficulty. Upon distillation in a vacuum (1 mm), it decomposes; therefore, the substance is hard to isolate in the pure form. The picrate was the only one of its salts we succeeded in preparing.



(I) (II) (III) (IV)

The product of complete hydrolysis – N-(β-carboxyethyl)-anabasine (IV) – was prepared by us by boiling of N-(β-propionitrile)-anabasine with a water-alcohol solution of barium hydroxide [4]. The yield was 35.3%.

Hydrolysis with hydrochloric acid [5] and barium aluminate [6] did not give positive results.

The barium salt of N-(β-carboxyethyl)-anabasine which is formed as a result of the reaction is stable in relation to carbonic acid, but is decomposed by hydrochloric acid. N-(β-Carboxyethyl)-anabasine was isolated in the free state from a solution of its hydrochloride by the method, proposed by Rodionov and Yartseva [7], in which ethylene oxide is used.

In order to examine the possibility of the direct synthesis of N-(β-carboxyethyl)-anabasine, the reaction between anabasine and acrylonitrile, in the presence of strong solutions of sodium hydroxide, was studied. An increase in the concentration of the alkali, without changing its total quantity, brought about a lowering of the yields of N-(β-propionitrile)-anabasine and partial hydrolysis to amino acids. On the carrying out of the reaction in the presence of a 40% aqueous solution of sodium hydroxide, N-(β-carboxyethyl)-anabasine is formed with yields up to 30%.

The methyl ester of N-(β-carboxyethyl)-anabasine (V) was obtained directly from anabasine and the methyl ester of acrylic acid. The yield was 96.2%.

(V)

EXPERIMENTAL

1. The preparation of N-(β-propionamide)-anabasine. 7 g of N-(β-propionitrile)-anabasine was introduced by drops into 35 ml of concentrated sulfuric acid, which was cooled externally with ice, and allowed to stand for 48 hours. Then, the mixture was diluted on cooling with 100 ml of water, neutralized with a 15% solution of

ammonia and evaporated over a water bath until dry. The reaction product was extracted with boiling benzene. After the distillation of the solvent, the residue crystallized on standing. The yield was 2.61 g (34.4%).

N-(β-Propionamide)-anabasine has a melting point of 105-106°, is quite soluble in benzene, alcohol, and water, and is difficultly soluble in petroleum ether, from which it was crystallized.

2.924 mg sub.: 0.470 ml N_2 (22°, 730 mm). 2.387 mg sub.: 0.376 ml N_2 (18°, 726 mm). Found %: N 17.87, 17.65. $C_{13}H_{19}ON_3$. Calculated %: N 18.01.

2. The preparation of N-(β-aminoethyl)-anabasine. 3.3 g of N-(β-propionamide)-anabasine was introduced in small portions into a cold solution of 7 g of potassium hydroxide in 15 ml of water and 1 ml of bromine. After the full dissolution of the amide, the solution was heated on a water bath at 80° for 4 hours. Then, after cooling, it was extracted with ether. The ether solution was boiled with activated charcoal, and the residue, after the driving off of the solvent, was dried in a vacuum desiccator. The yield was 1.34 g (46.0%).

The picrate of N-(β-aminoethyl)-anabasine was isolated on the addition of an aqueous solution of picric acid to the base in the form of a solidifying oil; after being washed several times with boiling alcohol and ground to a powder, the substance had a melting point of 199°.

3.924 mg sub.: 0.684 ml N_2 (20°, 709 mm). 3.005 mg sub.: 0.512 ml N_2 (20°, 710 mm). Found %: N 18.94, 18.54. $C_{12}H_{19}N_3 \cdot 3C_6H_3O_7N_3$. Calculated %: N 18.90.

3. The preparation of N-(β-carboxyethyl)-anabasine. 27.3 g of N-(β-propionitrile)-anabasine was dissolved in a saturated water-alcohol solution (2:3) of 10.0 g of barium hydroxide and boiled with a reflux condenser, over a water bath until the evolution of ammonia stopped, which required about 6 hours. After this, the alcohol was distilled off, and the residue was diluted with 100 ml of water and treated in a separatory funnel with ether. Then the aqueous solution of the barium salt of N-(β-carboxyethyl)-anabasine was acidified with a 10% solution of hydrochloric acid and evaporated over a water bath. The residue was purified by repeated treatment with anhydrous alcohol. The yield was 13.80 g (35.3%).

The dihydrochloride of N-(β-carboxyethyl)-anabasine is a strongly hygroscopic substance, which is crystallized from a mixture of dry acetone and anhydrous alcohol (3:1) on long external cooling with a mixture of calcium chloride and snow.

12 g of the dihydrochloride of N-(β-carboxyethyl)-anabasine in a 100 ml cylinder, was dissolved in 12 ml of water, and gaseous ethylene oxide was passed through, with external cooling with ice, until the increase in the volume was equal to 65 ml (about 60 g of ethylene oxide). Then the contents of the cylinder were decanted in an autoclave with a volume of 100 ml. The closed autoclave was maintained at a temperature of 0° for a week (until a negative reaction for the chlorine ion). After the evaporation of the excess ethylene oxide in a porcelain dish, the N-(β-carboxyethyl)-anabasine was extracted with chloroform. After the distillation of the chloroform, the residue, which had crystallized, was purified by recrystallization from a mixture of benzene and alcohol.

N-(β-Carboxyethyl)-anabasine was crystallized in the form of soft silky needles, with a melting point of 199°; it is quite soluble in chloroform, alcohol, partially soluble in water, and difficultly soluble in benzene and petroleum ether.

3.005 mg sub.: 0.310 ml N_2 (19°, 727 mm). Found %: N 11.54. $C_{13}H_{18}O_2N_2$. Calculated %: N 11.95.

4. The addition of ethyl cyanide to anabasine in the presence of 40% sodium hydroxide. To an emulsion of 11.8 g of anabasine and 1.0 g of a 40% solution of sodium hydroxide (0.4 g of NaOH), was added 5.0 ml of acrylonitrile. The mixture was heated in a sealed ampoule at 100° for 4 hours. After cooling, the mixture was washed in a separatory funnel several times with water. The residue — an oil — was dissolved in ether and dried over potash. After driving off of the solvent, 8.29 g (53%) of N-(β-propionitrile)-anabasine was obtained. The wash water was decanted, washed with ether, acidified with a 15% solution of hydrochloric acid, and evaporated until dry. 6.06 g of the dihydrochloride of N-(β-carboxyethyl)-anabasine was obtained (30%).

5. The interaction of anabasine with the methyl ester of acrylic acid.* A mixture of 10.0 g (0.061 mole) of anabasine and 5.5 g (0.064 mole) of the methyl ester of acrylic acid was heated in a sealed ampoule at 100° for 4 hours, and after cooling was distilled in vacuum. The obtained substance boiled at 189-192° (30 mm); 14.7 g (96.2%) was obtained.

* M. Yusupov participated in the carrying out of this experiment.

The dipicrate of the methyl ester of N-(β carboxyethyl)-anabasine was precipitated on the addition of an aqueous solution of picric acid to an alcohol solution of the base; after recrystallization from aqueous alcohol, the substance had a melting point of 140-141°.

2.753 mg sub.: 0.390 ml N_2 (21°, 720 mm). 2.794 mg sub.: 0.396 ml N_2 (19°, 732 mm). Found %: N 15.58, 15.56. $C_{14}H_{22}N_2 \cdot 2C_6H_3O_7N_3$. Calculated %: N 15.86.

Under analogous conditions, the reaction of anabasine with the methyl ester of methacrylic acid did not take place successfully.

SUMMARY

1. The conditions of the hydrolysis of N-(β -propionitrile)-anabasine have been studied. The compounds N-(β -propionamide)-anabasine and N-(β -carboxyethyl)-anabasine were prepared and characterized for the first time. From N-(β -propionamide)-anabasine, N-(β -aminoethyl)-anabasine was obtained.

2. It has been shown, that on carrying out the reaction of the addition of ethyl cyanide to anabasine in the presence of strong solutions of alkali, N-(β carboxyethyl)-anabasine is formed along with N-(β -propionitrile)-anabasine.

3. The reaction of anabasine with the methyl ester of acrylic acid has been studied for the first time; the methyl ester of N-(β -carboxyethyl)-anabasine has been isolated and characterized in these experiments.

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* See Consultants Bureau Translation, page 753.

THE SYNTHESIS OF 4(5)-IMIDAZOLECARBOXYLIC ACID

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4(5)-Imidazolecarboxylic acid is of interest for the synthesis of medicinal substances. Some of its simplest derivatives have interesting physiological properties. The acid itself may serve as a raw material for the synthesis of purine bases – caffeine, theobromine and others. The properties of 4(5)-imidazolecarboxylic acid have been insufficiently studied.

Preparation of 4(5)-imidazolecarboxylic acid was first described by Knoop in 1907 [1]. Windaus and Ulrich obtained it on the oxidation of glucose with a cuprammonium solution over the course of 3 years [2]. The high cost of the histidine as a starting substance in Knoop's synthesis, and the length of the process of oxidation in the synthesis of Windaus and Ulrich, explain the fact that these two methods were of only theoretical interest.

Pyman [3], and then Weidenhagen and Wegner [4], published a method for the oxidation of 4(5)-hydroxymethylimidazole to 4(5)-imidazolecarboxylic acid through the use of dilute nitric acid. Both methods may have preparative significance under conditions of the availability of the starting substance. We had previously worked out a simple method for the preparation of 4(5)-hydroxymethylimidazole from inexpensive substances – sugar, ammonia, and cupric carbonate [5]. However, the isolation and purification of it still remains complicated.

In the present work, a method for the preparation of 4(5)-imidazolecarboxylic acid, which is based on the oxidation of 4(5)-hydroxymethylimidazole, is proposed. Unlike the methods proposed earlier, the isolation of the intermediate product was not carried out in this process.

A mixture of different derivatives of imidazole, which is contained in the mother liquor after the decomposition of the copper complex and the isolation of the copper, was subjected to oxidation. This considerably simplified the process of the preparation of the acid and lowered the losses connected with the isolation and purification of 4(5) hydroxymethylimidazole.

The methyl and ethyl esters of the acid were prepared for its identification.

EXPERIMENTAL

The Preparation of 4(5)-Imidazolecarboxylic Acid

To a solution of 180 g of sugar in 600 ml of water, was added 5 ml of sulfuric acid; after heating for two hours on a water bath at 50-60°, the reaction mixture was allowed to stand overnight at room temperature. To the invert sugar formed in this way, was added a mixture of 222 g of basic cupric carbonate (malachite), 800 ml of ammonia, 30 ml of water, and 100 ml of formalin. The mixture was heated to boiling on a water bath, and then air was bubbled through it for 4 hours while the heating was continued.

On the cooling of the copper complex, the derivatives of imidazole were filtered and washed on the filter with 3% ammonia and water, until the decolorization of the wash water took place. The moist complex was shaken in 1 liter of water, 100 ml of hydrochloric acid (d 1.19) was added to the mixture, and then a saturated solution of sodium sulfide was added in small portions until the precipitation of the copper was completed. The copper sulfide precipitate was filtered, and the dark-brown mother liquor was evaporated on a water bath to $\frac{1}{4}$ of the original volume. The obtained solution was mixed with 350 ml of nitric acid (d 1.37), and the mixture was heated in a flask over a water bath for 3-4 hours.

The yellowish solution, which had become clear, was transferred to a porcelain dish and evaporated over the water bath until dry. The crystalline mass which was formed consisted mainly of a mixture of inorganic salts and 4(5)imidazolecarboxylic acid. The extraction of the acid from this mixture may be accomplished in two ways.

According to the first method, ammonia was added to the dry crystalline residue until the reaction showed a strong basic reaction to litmus. The excess ammonia was neutralized with acetic acid, and the mixture was evaporated over a water bath until dry. The dry residue was transferred into a Soxhlet apparatus and the acid was extracted with anhydrous alcohol. After the alcohol was driven off, the damp 4(5)-imidazolecarboxylic acid was recrystallized from alcohol. The yield was 28.4 g. The melting point of the substance is 284°.

According to the second method, a dry mixture of inorganic salts and 4(5)-imidazolecarboxylic acid was dissolved in the minimum amount of water and neutralized with a saturated solution of soda until it gave a neutral reaction to litmus, whereupon the main part of the 4(5)-imidazolecarboxylic acid was precipitated. The acid was separated, washed with a small amount of cold water, and recrystallized from water. The yield was 26.8 g. The melting point of the substance was 283-284°.

The Preparation of the Esters of 4(5)-Imidazolecarboxylic Acid

For the preparation of the ethyl ester of 4(5)-imidazolecarboxylic acid, 100 g of anhydrous alcohol was saturated with dry hydrogen chloride, and 10 g of 4(5)-imidazolecarboxylic acid was introduced into the reaction mixture. The solution was boiled over a water bath with a reflux condenser for 4 hours. The alcohol was then distilled off, and the dry residue was dissolved in a small amount of water and neutralized with a saturated solution of soda, litmus being used as the indicator. The ester, which was precipitated, was isolated, washed with water, and recrystallized from alcohol. The yield of the ethyl ester of 4(5)-imidazolecarboxylic acid was 9.3 g (74%). Its melting point was 160-162°.

6.985, 5.855 mg sub.: 13.135, 11.015 mg CO_2; 3.65, 3.097 mg H_2O. Found %: C 51.32, 51.30, H 5.85, 5.92. $C_6H_8O_2N_2$. Calculated %: C 51.42; H 5.75.

The ester was prepared with the same results, on the esterification of 4(5)-imidazolecarboxylic acid with sulfuric acid.

The methyl ester was prepared under analogous conditions. From 10 g of 4(5)-imid azolecarboxylic acid was separated 9.0 g of the ester. (71%, calculated on the 4(5)-imidazolecarboxylic acid). The melting point of the ester was 154-156°.

3.950, 4.882 mg sub.: 6.868, 8.508 mg CO_2; 1.747, 2.207 mg H_2O. Found %: C 47.45, 43.56; H4.95, 5.06. $C_5H_6O_2N_2$. Calculated %: C 47.56; H 4.80.

The properties of 4(5)-imidazolecarboxylic acid and its esters coincided with the literature data.

SUMMARY

A simple method for the preparation of 4(5)-imidazolecarboxylic acid from invert sugar has been developed.

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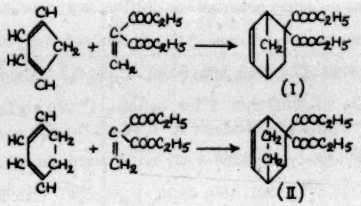
BARBITURIC ACIDS

III. THE METHYLENE-MALONIC ESTER IN DIENE SYNTHESIS. THE PREPARATION OF BARBITURIC ACIDS OF THE SPIRAN TYPE

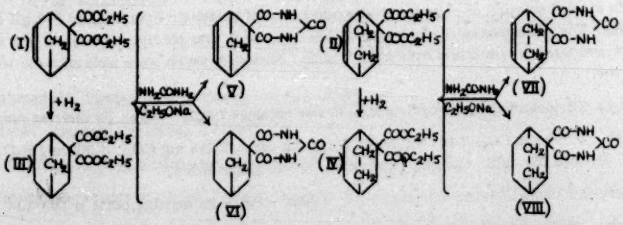
R. Ya. Levina and N. N. Godovikov

The use of methylene-malonic ester in the diene synthesis has been described only by Bachman and Tanner [1]* who studied the polymerization of this ester and its copolymerization with other unsaturated compounds. In the present work the reactions of methylene-malonic ester with cyclopentadiene and cyclohexadiene have been studied:



The products of these reactions — 1,1-dicarbethhoxy-2,2-endomethylenecyclohexene-3 and 1,1-dicarbethoxy-2.5-endoethylene cyclohexene-3 (yields of 60 and 27% respectively) were converted by hydrogenation into the corresponding saturated esters: 1,1-dicarbethoxy-2,5-endomethylene cyclohexane (III) and 1,1-dicarbethoxy-2,5-endoethylene cyclohexane (IV).

From all of the synthesized esters, which were identified by conversion into easily crystallizing dibasic acids, and which are disubstituted malonic esters, barbituric acids of a new type, which had not been previously described in the literature, were obtained, by interaction with urea, in the presence of sodium ethylate; the new type of barbituric acid is "spirobarbituric" acid, with an endomethylene and an endoethylene bridge in the carbocyclic radical ("bridge spirobarbituric" acids):



* In Holmes' review[2] this unique work is not mentioned.

The esters of unsaturated and saturated acids, and the dibasic acids and barbituric acids corresponding to them, which we have synthesized in the present work, have not been described in the literature previously.

EXPERIMENTAL

Methylene-malonic ester [3,4,5]. A mixture of 200 g of malonic ester, 93 g of 40% formalin and 3.2 g of diethylamine were heated on a strongly boiling water bath for 3 hours, after which the lower layer was separated and was distilled in a vacuum (in the distillation column, 0.1-0.2 g of potassium hydroxide was introduced).

The obtained methylene-malonic ester, which was distilled at 160-163° (7mm), and which had fully polymerized on the following day, was washed with ether. 150 g (70%) of polymer of methylene-malonic ester, in the form of a powder was isolated; it melted at 154-156°. According to the literature data [6], the melting point is 154-156°.

The interaction of methylene-malonic ester with cyclopentadiene and cyclohexadiene was carried out by the following method: The solid polymer (19 g; 0.11 mole) was depolymerized on heating to 220-240° in a Wurtz flask; the monomer of methylene-malonic ester which was formed under these conditions (17 g; 0.1 mole) was distilled in the reaction flask, where 15 ml of anhydrous benzene had been placed. On the completion of the depolymerization, the dienic hydrocarbon (0.2 mole) – cyclopentadiene or cyclohexadiene – was added to the distilled methylene-malonic ester, and the reaction mixture was heated for 6 hours* on a water bath, after which the benzene was distilled off, and the oil which remained was distilled in a vacuum.

1,1-dicarbethoxy-2,5-endomethylene-cyclohexene-3 (I) was obtained; the yield was 60%.

B.p. 129-130° (10 mm), n_D^{20} 1.4722, d_4^{20} 1.0952, MR_D 60.46. $C_{13}H_{18}O_4$. Calculated 60.67.

5.015 mg sub.: 12.055 mg CO_2; 3.510 mg H_2O. 7.230 mg sub.: 17.280 mg CO_2; 4.920 mg H_2O. Found %: C 65.33, 65.52; H 7.83, 7.62. $C_{13}H_{18}O_4$. Calculated %: C 65.52; H 7.59.

1,1-Dicarbethoxy-2,5-endoethylene-cyclohexene-3 (II) was obtained; the yield was 27%.

B.p. 135-136° (7 mm), n_D^{20} 1.4722, d_4^{20} 1.1201, MR_D 63.05. $C_{14}H_{20}O_4$. Calculated 63.18.

5.270 mg sub.: 12.886 mg CO_2; 3.815 mg H_2O. 4.780 mg sub.: 11.702 mg CO_2; 3.502 mg H_2O. Found %: C 66.66, 66.75; H 8.04, 8.14. $C_{14}H_{20}O_4$. Calculated %: C 66.64; H 8.01.

The hydrogenation of the obtained unsaturated esters (I and II) was carried out in the cold in a medium of absolute ethyl alcohol, in the presence of skeletal nickel. After the completion of hydrogenation (about 20 minutes later), the catalyst was separated, the alcohol distilled off, and the hydrogenated ester vacuum distilled.

1,1-Dicarbethoxy-2,5-endomethylene-cyclohexane (III) was obtained; the yield was 80%.

B.p. 124-125° (6 mm), n_D^{20} 1.4595, d_4^{20} 1.0754, MR_D 61.17. $C_{13}H_{20}O_4$. Calculated 61.14.

1,1-Dicarbethoxy-2,5-endoethylenecyclohexane (IV) was obtained; the yield was 83%.

B.p. 143-144° (8 mm), n_D^{20} 1.4648, d_4^{20} 1.0751, MR_D 65.43. $C_{14}H_{22}O_4$. Calculated 65.76.

The hydrolysis of the obtained unsaturated (I and II) and saturated (III and IV) esters to the corresponding dibasic acids was carried out according to the following method: the ester (0.01 mole) was gently heated on a water bath with an alcohol solution of potassium hydroxide (1.2 g of potassium hydroxide in 6-7 ml of ethyl alcohol) for 1.5-2 hours. The potassium salt, which is insoluble in alcohol, was precipitated out; it was then filtered, washed with ether, and treated with dilute hydrochloric acid. The acids which were isolated were recrystallized from aqueous alcohol.

1,1-Dicarboxy-2,5-endomethylene-cyclohexene-3 was obtained (yield – 73%); its melting point is 122-123°.

4.496 mg sub.: 9.773 mg CO_2; 2.441 mg H_2O. 3.642 mg sub.: 7.915 mg CO_2; 1.931 mg H_2O. Found %: C 59.32, 59.31; H 6.07, 5.93. $C_9H_{10}O_4$. Calculated %: C 59.31; H 5.87.

1,1-Dicarboxy-2,5-endoethylenecyclohexene-3, (yield – 65%); its melting point is 163-164°.

7.548 mg sub.: 16.982 mg CO_2; 4.275 mg H_2O. 4.543 mg sub.: 10.354 mg CO_2; 2.612 mg H_2O. Found %: C 61.21, 61.44; H 6.23, 6.32. $C_{10}H_{12}O_4$. Calculated %: C 61.20; H 6.17.

* The depolymerization and the reaction with the diene were carried out in a stream of nitrogen, in order to avoid the polymerization of the monomer.

1,1-Dicarboxy-2,5-endomethylene-cyclohexane (yield – 60%); its melting point is 174-175°.

5.310 mg sub.: 11.940 mg CO_2; 3.092 mg H_2O. 5.390 mg sub.: 12.133 mg CO_2; 3.194 mg H_2O. Found %: C 61.36, 61.43; H 6.65, 6.61. $C_9H_{12}O_4$. Calculated %: C 61.45; H 6.57.

1,1-Dicarboxy-2,5-endoethylenecyclohexane (yield – 60%); its melting point is 159-160°.

5.530 mg sub.: 12.217 mg CO_2; 3.615 mg H_2O. 5.868 mg sub.: 12.938 mg CO_2; 3.818 mg H_2O. Found %: C 60.29, 60.17; H 7.31, 7.28. $C_{10}H_{14}O_4$. Calculated %: C 60.59; H 7.12.

Spiro-barbituric acids. 4 g of urea (0.07 mole) was added to sodium alcoholate (0.7 g Na in 20 ml of absolute alcohol), and then the corresponding saturated or unsaturated ester (0.01 mole) was added. The reaction mixture was heated at 100-110° for six hours. The sodium salt of the spiro-barbituric acid precipitated out; it is insoluble in alcohol; it was filtered, washed with alcohol, ether, and dried in the air. After acidification with dilute hydrochloric acid, spiro-barbituric acid was isolated; it was recrystallized from dilute alcohol.

The constants, yields, and analytical data on the obtained "bridge spiro-barbituric" acids are given in the table.

TABLE

"Bridge Spiro barbituric" Acids

Obtained	Formula	Melting point	Yield (%)	Nitrogen content (%)	
				found	calculated
From methylene-malonic ester and cyclopentadiene	(V)	Decompn. without melting at ~300°*	50	13.92, 14.00	13.49
From methylene-malonic ester and cyclohexadiene	(VI)	248-250	52	13.17, 13.13	12.67
From the hydrogenated product of methylene-malonic ester and cyclopentadiene	(VII)	228-230	98-99	13.88, 13.96	13.43
From the hydrogenated product of methylene-malonic ester and cyclohexadiene	(VIII)	272-273	98-99	12.70, 12.79	12.60

SUMMARY

1. The "diene synthesis" between cyclic dienes (cyclopentadiene and cyclohexadiene) and methylene-malonic ester has been accomplished for the first time.

2. The corresponding saturated esters (1,1-dicarbethoxy-2,5-endomethylene-cyclohexane and 1,1-dicarbethoxy-2,5-endoethylenecyclohexane were obtained by the hydrogenation of the products of these reactions (1,1-dicarbethoxy-2,5-endomethylene-cyclohexene-3, and 1,1-dicarbethoxy-2,5-endoethylene-cyclohexene-3).

3. From all of the synthesized esters (identified by conversion into crystalline dibasic acids) we obtained, by the action of urea in the presence of sodium ethylate, barbituric acids of a type which had not been described in the literature – "bridge spiro-barbituric" acids. All of the compounds obtained in this work have been described for the first time.

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* This barbituric acid and its sodium salt darken in the air.

INVESTIGATIONS IN THE FIELD OF MOLECULAR CHROMATOGRAPHY

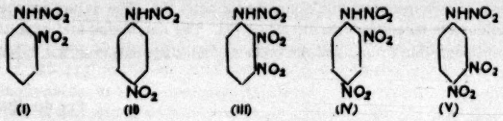
II. THE SEPARATION OF MIXTURES OF NITROPHENYLNITRAMINES

K. A. Ogloblin and G. V. Markina

There is no data in the literature on the utilization of the chromatographic method for the purification and separation of mixtures of nitrophenylnitramines. There is also no literature data on the separation of mixtures of nitrophenylnitramines by any other method.

Continuing out investigations in the field of chromatographic analysis, we considered it useful to fill this gap in the literature. In undertaking the investigation of the chromatographic separation of mixtures of nitrophenylnitramines, we set ourselves the goal of working out a method for such a separation. Nitrophenylnitramines are acids that are even stronger than nitrophenols; therefore, it was also of interest to clarify the question of whether or not there was a correspondence between the acidity and the adsorbability of nitrophenylnitramines, as was observed in the case of nitrophenols [1].

Several mixtures consisting of five nitrophenylnitramines were used for the investigation: o-nitrophenylnitramine (I), p-nitrophenylnitramine (II), 2,3-dinitrophenylnitramine (III), 2,4-dinitrophenylnitramine (IV), and 3,4-dinitrophenylnitramine (V).



In view of the fact that the chemistry of the nitrophenylnitramines has been insufficiently studied and in view of the insufficiently exact character of the literature data, it is necessary to dwell on some pecularities of the synthesis, purification and properties of these compounds.

Nitrophenylnitramines (I), (II), (III) and (V) were prepared by Macciotta's method [2, 3], and compound (IV) according to the method of Zincke and Kuchenbecker [4], after which they were purified chromatographically. As our investigations showed, on the synthesis of the nitramines by the indicated methods, it is necessary to keep in mind that these compounds are dissolved in water to a considerable extent, and that a large amount of the substance (for o-nitrophenylnitramine, more than 60%) may be isolated from aqueous solutions on synthesis. Disregarding of this fact, evidently, caused the statement of Macciotta [3], that compound (V) is obtained with very low yield, although we obtained it with a yield of 47%. No data is given in the literature in regard to the yields of the rest of the compounds, and there is no indication of the melting points of compounds (III) and (IV).

In spite of the existence of contrary opinions [3], nitramine (V) is a fully stable compound and may be stored without change for several months. The least stable of the synthesized nitramines is 2,3-dinitrophenylnitramine (III), which was decomposed on storing in an desiccator, over aluminum oxide in the light, in the course of several days, with the evolution of nitrogen oxides, and conversion into a dark, semi-liquid mass. As our observation showed, the decomposition of compound (III) was caused by the light, and the oxides of nitrogen which were formed as a result of the decomposition greatly accelerated the process. On the storing of compound (III) in beakers which were open to the air, in the dark, the nitramine was not noticeably changed over a period of ten days.

As a consequence of their great sensitivity to heat, the nitrophenylnitramines have been purified, up to the present time, mainly by means of recrystallization of their salts [5], or by means of substitution from salts by the action of strong mineral acids [2, 3].

Chromatographic purification of the nitrophenylnitramines has well-known advantages since it eliminates the necessity of preparing the salts and can be carried out with smaller losses. On the chromatographic purification of 2,3-dinitrophenylnitramine and on the separation of mixtures into whose composition it enters, the column should be wrapped in black paper, in order to prevent the decomposition of the substance due to the prolonged action of light.

A total of seven mixtures of nitramines, of the following compositions were investigated: 1) (I) + (II); 2) (I) + + (IV); 3) (II) + (IV); 4) (I) + (II) + (IV); 5) (IV) + (V); 6) (III) + (IV) + (V) and 7) (I) + (II) + (III) + (IV) + (V).

Just as in the case of the separation of mixtures of nitrophenols, aqueous aluminum oxide, which contained 14.3-15.5% water (drying at 110-115°) was used as an adsorbent; benzene, ether and their mixtures were used as solvents. The preparation of the adsorbent and the method of carrying out the experiments have been described earlier [1].

It turned out that the relative order of the adsorption of each of the investigated nitramines, in relation to the other nitramines in the mixture, remained the same regardless of the number of components in the mixture. Thus, for example, p-nitrophenylnitramine (II) in all cases showed the least adsorbability, that is, it was always found in the very bottom of the column. The decomposition of the nitramines in the chromatographic column made it possible for us to distribute them in the following adsorption series (in order of increasing adsorbability):

$$(II) < (I) < (V) < (IV) < (III).$$

In order to clarify the question as to whether or not there was the same dependence between adsorbability and acidity in the case of the nitrophenylnitramines as in the case of the nitrophenols, it was necessary to compare the obtained adsorption series of the nitrophenylnitramines with the order of change of their dissociation constants.

According to the literature data, of the five compounds studied, dissociation constants had been measured only for compounds (I) and (II) [5]. In order to evaluate the comparative acidity of compounds (III), (IV) and (V), and to calculate their dissociation constants, it seemed to us that it was possible to utilize the linear equation, relating the dissociation constants of arylnitraminic and arylcarbonic acids [5]. The values for the dissociation constants of the dinitrobenzoic acids were taken from the literature [6]. The calculated and experimental values for the dissociation constants of nitrophenylnitramines and the order of their distribution in the column are given in the table.

TABLE

Name of compound	Order of distribution in the column (from the bottom up)	Value of the dissociation constant (15°)
o-Nitrophenylnitramine (I)	2	$1.32 \cdot 10^{-3}$ [5]
p-Nitrophenylnitramine (II)	1	$1.12 \cdot 10^{-4}$ [5]
2,3-Dinitrophenylnitramine (III) . . .	5	$3.46 \cdot 10^{-3}$*
2,4-Dinitrophenylnitramine (IV) . . .	4	$8.86 \cdot 10^{-3}$*
3,4-Dinitrophenylnitramine (V) . . .	3	$4.31 \cdot 10^{-4}$*

For the first five mixtures the order of adsorption of the nitrophenylnitramines, just as in the case of the nitrophenols [1], corresponds to the order of change of their dissociation constants. For the last mixtures such a correspondence between the adsorbability and acidity is not observed in two cases. In the sixth mixture, 2,3-dinitrophenylnitramine (III) is adsorbed more strongly than 2,4-dinitrophenylnitramine (IV), although the acidity of the latter is greater; in the seventh mixture, 3,4-dinitrophenylnitramine (V) is adsorbed more strongly than o-nitrophenylnitramine (I), although the dissociation constant of the latter is higher.

Keeping in mind the complicated nature of the process of adsorption, it would be difficult to expect a full correspondence between the changes of adsorbability and changes in the values of the dissociation constants in all cases. The acidity of compounds is only one of the active factors which determine adsorbability. The other factor, which, for example, in the case of compounds (I) and (V) may play an essential role, is the solubility. Thus, we found that the solubility of compound (I) is ether is approximately seven times greater than the solubility of compound (V). As a consequence of this, regardless of the greater value of its dissociation constant, o-nitrophenylnitramine (I) was washed out of the column more quickly than 3,4-dinitrophenylnitramine (V). A similar relationship was also observed earlier [1], on the comparison of the acidity and adsorbability of o-nitrophenol and m-nitrophenol

* Calculated values, see [5].

EXPERIMENTAL

1. The Syntheses and Chromatographic Purification of Nitrophenylnitramines*

a) o-Nitrophenylnitramine (I). From 15 g of o-nitroaniline (melting point 71-73°) in a solution of 150 ml of glacial acetic acid, 18 ml of nitric acid (d 1.51, freed of nitrogen oxides [7]) and 19 ml of acetic anhydride with a boiling point of 138-141°, after the decantation of the reaction products on ice, filtration with suction (filtrate I), washing with water, dissolution of the precipitate in a 3% soda solution, precipitation from the soda solution with 2 N hydrochloric acid, filtration with suction (filtrate II), washing with water and drying, was obtained 4.63 g (23.3%) of o-nitrophenylnitramine, with a melting point of 64.5-65.5°. From filtrate I, which remained in solution, the nitramine was extracted with benzene, and the benzene solution was washed with water and shaken with a 3% soda solution. On the acidification of the aqueous alkaline solution, the nitramine precipitated in the form of a light yellow oil, which quickly crystallized. The crystals were washed with water and dried in a vacuum desiccator over calcium chloride; the weight of the crystals was 5.80 g (29.2%), their melting point was 66.3-66.7°. By the same method, 3.92 g (19.7%) of a nitramine with a melting point of 65.7-67.3° was isolated from filtrate II. The total yield of o-nitrophenylnitramine was 14.35 g (72.2%). Thus, from the aqueous solution, more than two-thirds of the total quantity of the nitramine was extracted.

The chromatographic purification of o-nitrophenylnitramine. A solution of 1.0 g of o-nitrophenylnitramine in 20 ml of benzene was passed through a column 365 by 12 mm. The adsorbent – moistened aluminum oxide** – loses 20.5-20.6% of its weight on roasting (550-600°), and 14.2-14.3% on drying (110-115°). The column was washed with 40 ml of benzene, the excess pressure in the apparatus was 40 mm, and the temperature was 15°. From the main greenish yellow zone, of a width of 164 mm, on working with a mixture of benzene and dilute hydrochloric acid, 0.88 g of yellow flaky crystals precipitated; their melting point was 66.5-67.5°.

Literature data: melting point 65.5-66° [5], 65.5° [8].

b) p-Nitrophenylnitramine (II). From 20 g of p-nitroaniline (melting point 147-148°), 150 ml of glacial acetic acid, 25 ml of nitric acid (d 1.51, free of nitrogen oxides) and 25 ml of acetic anhydride, according to the preceding method, was obtained 13.72 g (51.8%) of p-nitrophenylnitramine, with a melting point of 110-112°. From the aqueous solutions it was possible to extract with ether supplementary amounts of p-nitrophenylnitramine.

The chromatographic purification of p-nitrophenylnitramine. A solution of 2.0 g of p-nitrophenylnitramine with a melting point of 110-112° in 220 ml of benzene was passed through a column 288 by 13 mm; the adsorbent was moistened aluminum oxide, as in the preceding experiment. The column was washed with 30 ml of benzene and 120 ml of a mixture of benzene and ether (1:1), at an excess pressure of 60 mm and a temperature of 19°. From the main greenish-yellow zone, of a width of 282 mm, on working with a mixture of benzene and dilute hydrochloric acid, 0.96 g of fine light-yellow crystals was extracted; their melting point was 113.7-114.3° (at 115° they decompose). From the filtrate which was run out of the column, an additional 0.56 g of substance with a melting point of 112.5-113° was extracted. A total of 1.52 g of p-nitrophenylnitramine was isolated.

The literature data gives a melting point of 112-113° [5], 110-111° [9].

c) 2,3-Dinitrophenylnitramine. The 2,3-dinitroaniline, which served as the starting material for the synthesis of the nitramine, was obtained by the method of Van de Vliet [10]. From 2.7 g of 2,3-dinitroaniline (melting point 124.5-125°) by the method of Macciotta [3], was obtained 1.70 g of the nitramine with a melting point of 62.5° (violent decomposition). From aqueous solutions of benzene was extracted 0.78 g more of the nitramine, with a melting point of 63.5°. A total of 2.48 g (73.8%) of 2,3-dinitrophenylnitramine. In the work of Macciotta [3], the yield of the product and its melting point are not given. Freshly prepared 2,3-dinitrophenylnitramine is a light-yellow crystalline substance, which becomes bright orange in color after several days, if it is stored in an desiccator over anhydrous aluminum oxide in the light; in this case, the oxides of nitrogen are evolved. The process of decomposition is completed after several days. The partial decomposition of the nitramine was also observed in the process of chromatographic analysis on aqueous aluminum oxide, which is shown by the darker coloration of the zone of the nitramine on the side which is turned toward the light. On storing in the dark, in an open beaker, the nitramine did not undergo noticeable decomposition over a period of ten days.

From the yellow aqueous solutions of the nitramine, on the action of silver nitrate, the difficultly soluble silver salt was isolated, in the form of fine colorless shining crystals, which settled on the bottom of the reaction vessel.

* In view of the inexactness of the literature data [2, 3, 4], the syntheses of the nitrophenylnitramines are described.

** For the preparation of the aluminum oxide and the extraction of the nitramines from the adsorbent, see [1].

The chromatographic purification of 2,3-dinitrophenylnitramine. 0.7 g of the nitramine in 150 ml of benzene was passed through a column 260 by 22 mm containing moistened aluminum oxide (for each 100 g of commercial aluminum oxide, 20 g of water was added; this corresponds to about 17% moisture). The column was washed with 20 ml of benzene and 270 ml of ether, the excess pressure in the apparatus was 40 mm, and the temperature was 19°.

From the main light-yellow zone, of a width of 30 mm, on working with a mixture of benzene and dilute hydrochloric acid, 0.48 g (about 70%) of the substance was extracted in the form of clear, light-brown flat triangles with a melting point of 67° (violent decomposition). In connection with the low stability of the nitroamine in relation to light and heat, its melting point in various experiments varied between 62-72°. In order to prevent the decomposition of the nitramine during the chromatographic purification, the column should be protected from the action of light with black paper.

The equivalent of the synthesized nitramine was determined by neutralization: a charge of the nitramine was dissolved in a mixture of 15 ml of alcohol and 10 ml of water and titrated with an alcohol solution of potassium hydroxide in the presence of alkaline blue 6B (from dark green to dark red-green).

0.0980 g sub.: 4.27 ml 0.1 N KOH. 0.1002 g sub.: 4.38 ml 0.1 N KOH. Found: equiv. 229.5, 228.6. $C_6H_4O_8N_4$. Calculated: equiv. 228.1.

d) 2,4-Dinitrophenylnitramine. In the article by Zincke and Kuchenbecker [4], there are indications that 2,4-dinitrophenylnitramine may be prepared with good yields on the introduction of p-nitroaniline into nitric acid at −15°, (a yield of 3 g from 5 g of p-nitroaniline, that is, 36.4%). Since these authors did not give a description of the synthesis, we will describe the synthesis of 2,4-dinitrophenylnitramine, obtained with a yield of 65.2%.

5 g of the dry, finely ground p-nitroaniline was introduced in small portions during 35-40 minutes into 50 ml of nitric acid (d 1.51, free of nitrogen oxides), cooled to −13°; thereupon, a small rise in temperature took place (not higher than −10°). The dark-brown clear liquid was decanted into 1.2-1.4 liters of ice and free of water. The dirty-yellow precipitate which was obtained was isolated, washed with water (filtrate I), and dissolved in a 3% soda solution (about 500 ml); the red soda solution was acidified with 2 N hydrochloric acid (according to a Congo red indicator), and the fine, dirty-yellow precipitate was isolated, washed with water (filtrate II), laid out on a porous dish and dried in a desiccator over calcium chloride for two days. The product weighed 3.02 g. and melted at 99-102.5° (it decomposed at 105°). From filtrate II, 1.05 g of a substance with a melting point of 99-100° was extracted with ether. The total yield was 5.38 g (65.2%).

The chromatographic purification of 2,4-dinitrophenylnitramine. A solution of 1.29 g of the nitramine in 70 ml of benzene was passed through a column 286 by 14 mm containing moistened aluminum oxide (15.5% moisture at 110-115°). The column was washed with 30 ml of benzene and 20 ml of ether, at an excess pressure of 60 mm and a temperature of 17°. From the main greenish-yellow zone, of a width of 108 mm, was extracted, on working with a mixture of benzene and hydrochloric acid, 1.19 g of crystals in the form of long, thick rods, which were yellow-brown in color; their melting point was 103.3-104°.

The neutralization equivalent was determined as in the case of 2,3-dinitrophenylnitramine.

0.1112 g sub.: 4.84 ml 0.1 N alcoholic KOH. 0.1206 g sub.: 5.30 ml 0.1 N alcoholic KOH. Found: equiv. 229.9, 227.4. $C_6H_4O_8N_4$. Calculated: equiv. 228.1.

According to the literature data [4], the melting point is 101° (with decomposition).

e) 3,4-Dinitrophenylnitramine. 3,4-Dinitroaniline — the starting material for the synthesis of the nitramine — was prepared by the method of Van de Vliet [10]. The 3,4-dinitrophenylnitramine was prepared by Macciotta's method [3]. The latter indicates that the yield of the nitramine is very low, that the substance does not melt, and is unstable. But 3,4-dinitrophenylnitramine was prepared by us with a yield of about 50% and was a fully stable product under ordinary conditions; we, therefore, consider it useful to describe the synthesis of the nitramine.

4 g of 3,4-dinitroaniline (melting point 148-150°) was dissolved with heating in 90 ml of glacial acetic acid. The solution was cooled enough so that the acetic acid was not crystallized, and 5 ml of nitric acid (d 1.51, free of nitrogen oxides) was gradually added to it, whereupon, toward the end of the addition, a small amount of a crystalline precipitate was separated out. After this, 5 ml of acetic anhydride was gradually added to the reaction mixture; the evolution of heat was not observed in this process. The precipitate was dissolved, and the color of the solution changed after 10 minutes from brown-orange to orange-yellow. After 20 minutes the reaction mixture

was decanted on ice, and a turbid yellow solution was obtained. On the addition of water and ice, the turbidity was increased, but there was no precipitate. 6 benzene extracts were made from the solution; they were dried off with anhydrous sodium sulfate, the benzene was vacuum distilled and the remants of the benzenewere evaporated under a hood. 2.34 g (47%) of dirty-yellow crystals with a reddish tint were obtained.

The chromatographic purification of 3,4-dinitrophenylnitramine. A solution of 2.34 g of the nitramine in 45 ml of dry ether was passed through a column 218 by 22 mm. The adsorbent was prepared by the moistening of clear aluminum oxide (25 ml of water per 100 g of the oxide, which corresponds to about 20% moisture). The column was washed with 330 ml of dry ether, at an excess pressure in the apparatus of 20 mm, and a temperature of 22°. From the main greenish-yellow zone, of a width of 115 mm, was isolated, on working with a mixture of benzene and dilute hydrochloric acid, 1.69 g of fine, yellowish crystals with a melting point of 82-82.5° (violent decomposition). From the greenish-yellow zone above the main one (its width was 25 mm) was isolated 0.47 g more of the nitramine in the form of gold-yellow, thin needles, which were attached to each other.

After the second purification on the same adsorbent, yellowish needles with a melting point of 94° were obtained (violent decomposition).

Depending on the length of heating in the apparatus, the melting point of the 3,4-dinitrophenylnitramine in the individual experiments varied between 81-97.5°, violent decomposition of the substance taking place immediately after melting.

The synthesized 3,4-dinitrophenylnitramine, like compounds (I)-(IV), showed a qualitative reaction for nitramines [11]. The neutralization equivilant was determined, just as in the preceding cases.

0.0951 g sub.: 4.20 ml 0.1 N alcoholic KOH. 0.1011 g sub.: 4.46 ml 0.1 N alcoholic KOH.
Found: equiv. 226.7, 226.8. $C_6H_4O_6N_4$. Calculated: equiv. 228.1.

II. The Separation of Mixtures of Nitrophenylnitramines

The arrangement of the apparatus, the preparation of the moistened aluminum oxide, the method of the carrying out of the experiments, and the means of extracting the adsorbed compounds from the adsorbent, after the zones had been mechanically separated from each other, have been described in the work on the separation of mixtures of nitrophenols [1]. All of the experiments were carried out at small excess pressures (20-60 mm) and at room temperature.

1) o-Nitrophenylnitramine (I) and p-nitrophenylnitramine (II). 0.10 g (I) and 0.10 g (II) in 30 ml of benzene, column – 128 by 14 mm, moisture content of the aluminum oxide, 14.2-14.3% (110-115°); washing – benzene 30 ml, a mixture of benzene with ether (1:1), 250 ml, pressure, 40 mm. In the column – two light-yellow zones with different greenish tints (from the bottom up): a width of 30 mm (the first fraction) and 32 mm (the second fraction), with a weakly marked light intermediate zone of a width of 2 mm. The zones were extracted with a spatula, and worked with a mixture of benzene and dilute hydrochloric acid. We isolated: the first fraction – light-yellow crystals, weight 0.06 g (60%) with a melting point of 112.5-113.5° (p-nitrophenylnitramine); the second fraction – light-yellow crystals, weight 0.07 g (70%), with a melting point of 61.5-62° (o-nitrophenylnitramine).

2) o-Nitrophenylnitramine (I) and 2,4-dinitrophenylnitramine (IV). 0.10 g (I) and 0.10 g (IV) in 30 ml of benzene, the column and adsorbent being the same as in the preceding experiment; the washing – with benzene, 70 ml, a mixture of benzene and ether (1:1) 350 ml; the pressure 40 mm. The following zones were formed (from the bottom up): light greenish-yellow, of a width of 22 mm (first fraction) and yellow, of a width of 13 mm (second fraction), with a white intermediate section between them of 2 mm. The following were isolated: the first fraction – crystals of a light-yellow color, weight, 0.08 g (80%), melting point 66-66.5° (o-nitrophenylnitramine); the second fraction – yellowish crystals, weight 0.08 g (80%), melting point 98.5-99.7°; a mixed sample with 2,4-dinitrophenylnitramine melted at 99.3 100°.

3) p-Nitrophenylnitramine (II) and 2,4-dinitrophenylnitramine (IV). 0.10 g (II) and 0.10 g (IV) in 40 ml of benzene, the column and adsorbent being the same as in the preceding experiments; the washing – benzene 40 ml, the mixtures of benzene with ether (4:1) 120 ml, (1:1) 80 ml; the pressure 40 mm. The following zones were fomred (from the bottom up): greenish-yellow, width 38 mm (first fraction) and greenish-yellow, 15 mm (second fraction), between them a white intermediate section (8 mm). The following substances were isolated: the first fraction – light-yellow crystals, weight 0.05 g (50%), melting point 113.5° (p-nitrophenylnitramine); the second fraction – light-yellow crystals, weight 0.08 g (80%), melting point 98.8-99.7° (2,4-dinitrophenylnitramine).

4) o-Nitrophenylnitramine (I), p-nitrophenylnitramine (II) and 2,4-dinitrophenylnitramine (IV). 0.10 g (I), 0.10 g (II) and 0.10 g (IV) in 30 ml of benzene, the column being 193 by 13 mm, the adsorbent as in the preceding experiments: the washing – mixture of benzene with ether (4:1) 50 ml, (1:1) 300 ml; the pressure 60 mm. Three main zones were formed, divided by white intermediate zones (from the bottom up): a greenish-yellow zone of a width of 45 mm (first fraction), a yellow-greenish zone, 25 mm (second fraction), and a yellow zone, 19 mm (third fraction). The following substances were isolated: first fraction – yellow crystals, weight 0.07 g (70%), melting point 113.5-114° (p-nitrophenylnitramine); the second fraction – yellow crystals, weight 0.06 g (60%), melting point 66-66.4°; a mixed sample with o-nitrophenylnitramine did not give a depression of the melting point; the third fraction – yellow crystals, weight 0.09 g (90%), melting point 58°. After two chromatographic separations on the same adsorbent, 0.06 g (60%) of a substance with a melting point of 98.5-100° was isolated; a mixed sample with 2,4-dinitrophenylnitramine did not give a depression of the melting point.

5) 2,4-Dinitrophenylnitramine (IV) and 3,4-dinitrophenylnitramine (V). 0.10 g (IV) and 0.10 g (V) in a mixture of 30 ml of benzene and 10 ml of ether, the column being 98 by 11 mm, the moisture content of the aluminum oxide being 15.5% (110-115°); washing – ether 210 ml, pressure 30 mm. The following zones were formed (from the bottom up): greenish-yellow, of a width of 35 mm (first fraction) and yellow-green, of a width of 18 mm (second fraction), divided by a narrow, light rose intermediate section. The following substances were isolated: the first fraction – fine, rigid crystals, gray-brown in color, weight 0.07 g (70%), melting point 81-81.5° (decomposition); a mixed sample with 3,4-dinitrophenylnitramine did not give a depression of the melting point; the second fraction – brown crystals, weight 0.08 g (80%), melting point 58-59°. After the chromatographic purification on the same oxide, 0.06 g (60%) of light yellow crystals with a melting point of 100.3-101.3° was isolated from ether; a mixed sample with 2,4-dinitrophenylnitramine did not give a depression of the melting point.

6) 2,3-Dinitrophenylnitramine (III), 2,4-dinitrophenylnitramine (IV) and 3,4-dinitrophenylnitramine (V). 0.10 g (III), 0.10 g (IV) and 0.10 g (V) in a mixture of 35 ml of benzene and 15 ml of ether, the column being 156 by 11 mm, the adsorbent as in the preceding experiment; the washing – ether, 200 ml, the pressure, 20 mm, the length of the experiment, 8 hours. Three main adjoining zones were formed (from the bottom up): greenish-yellow, of a width of 27 mm (first fraction), yellow green, 13 mm (second fraction) and greenish-yellow, 13 mm (third fraction). The zones were extracted, and the borderline parts were thrown out. The following substances were isolated in the usual way: the first fraction – dirty-yellow crystals, weight 0.07 g (70%), melting point 97.5° (violent decomposition), without a depression of the melting point with 3,4-dinitrophenylnitramine; the second fraction – light brown crystals, weight 0.06 g (69%), melting point 62-63°. After chromatographic purification on the same aluminum oxide, 0.05 g (50%) of a substance with a melting point of 99.7-100.5° was isolated; a mixed sample with 2,4-dinitrophenylnitramine did not give a depression of the melting point; the third fraction – light brown crystals, weight 0.08 g (80%), melting point 71°; a mixed sample with 2,3-dinitrophenylnitramine did not give a depression of the melting point.

Thus, the order of the adsorption of the dinitrophenylnitramines is: 3,4-< 2,4-< 2,3-dinitrophenylnitramine.

7) o-Nitrophenylnitramine (I), p-nitrophenylnitramine (II), 2,3-dinitrophenylnitramine (III), 2,4-dinitrophenylnitramine (IV) and 3,4 dinitrophenylnitramine (V). 0.10 g of each of the indicated nitramines in a mixture of 10 ml of benzene and 70 ml of ether, the column being 190 by 11 mm; the adsorbent as in the preceding experiment; the washing – 200 ml of ether, the pressure 20 mm, the length of the experiment – nine hours. The following adjoining zones were formed (from the bottom up): light yellow, 35 mm (first fraction), light yellow, 45 mm (second fraction), light yellow, 27 mm (third fraction), dirty-yellow, 22 mm (fourth fraction), dirty-orange, 17 mm (fifth fraction), and three narrow dark-brown zones at the very top of the column (sixth fraction). The following substances were isolated: the first and second fractions – light brown crystals, weight 0.075 g (75%), melting point 110-112°; a mixed sample with p-nitrophenylnitramine did not give a depression of the melting point; the third fraction – yellow crystals, weight 0.050 g (50%), melting point 65-65.5°; a mixed sample with o-nitrophenylnitramine did not show a depression of the melting point; the fourth fraction – light brown crystals, weight 0.094 g (94%), melting point 87.5° (violent decomposition); a mixed sample with 3,4-dinitrophenylnitramine did not show a depression of the melting point; the fifth and sixth fractions are a brown liquid, which was not crystallized on standing; it was a mixture of 2,3- and 2,4 dinitrophenylnitramines. It was not investigated further.

Thus, the order of adsorption for the five nitrophenylnitramines is: (II)<(I)<(V)< a mixture of (III) and (IV).

SUMMARY

1. The methods of the synthesis and isolation have been made more exact, and a method for the chromatographic purification of nitrophenylnitramines has been proposed.

2. The chromatographic separation from benzene and ether on aqueous aluminum oxide of seven artificial mixtures of nitrophenylnitramines has been carried out; the mixtures consisted of the following nitrophenylnitramines: o-, p-nitrophenylnitramine, 2,3-, 2,4- and 3,4-dinitrophenylnitramine.

3. It has been established that the adsorbability of the indicated compounds, under the conditions of the experiments, is determined to a considerable degree by their acidity.

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INVESTIGATIONS IN THE ANTHRAQUINONE SERIES

XXIV. THE HYDROLYSIS OF THE α-SULFO ACID OF ANTHRAQUINONE WITH THE SUBSTITUTION OF THE SULFO GROUP BY THE HYDROXYL GROUP•

V. V. Kozlov and A. A. Egorova

In our preceding article, we showed that in spite of the literature data on the impossibility of the hydrolysis of the α-sulfo acids of anthraquinone in the absence of mercury, such a hydrolysis of it in 70-80% sulfuric acid is fully possible and takes place exclusively in the direction of the ordinary replacement of the sulfo group by hydrogen, with the formation of anthraquinone.

In contrast to the generally accepted conditions for the carrying out of the hydrolysis in concentrated sulfuric acid, we carried out the hydrolysis of the α-sulfo acid of anthraquinone and its salts in dilute sulfuric acid and also in water in a closed system, that is, in sealed tubes at high temperatures.

The experiments on the heating of the α-sulfo acid of anthraquinone in a sealed tube with water (0.72 g – 0.0025 mole – of the sulfo acid in 25 ml of water) led to results [1] that were different from the ordinary course of the hydrolysis reaction.

It turned out that under the action of water at 180-300°, the α-sulfo acid of anthraquinone is smoothly converted, after six hours, into α-hydroxy anthraquinone, with a yield of the latter from 7-90% [2, 1a] (see Table 1).

In the reaction medium, there remains the unchanged α-sulfo acid, which is identified by the ordinary means of its conversion into α-chlorcanthraquinone. It has been established that at 100°, the hydrolysis of the α-sulfo acid of anthraquinone with water does not take place, even on heating for twenty-four hours. The conversion of the α-sulfo acid of anthraquinone to α-hydroxyanthraquinone depends not only on the temperature, but also on the time, the pressure and the volume of water, (Table 2). The experimental heating of the α-sulfo acid of anthraquinone in an open system, with a continuous stream of superheated steam at 170-250°, over a period of six hours, did not lead to the formation of the products of hydrolysis or to a change in the substance. In the reaction medium on the conversion of the α-sulfo acid in water, in sealed tubes, the presence of sulfurous acid has always been established, it being 80% oxidized to sulfuric acid under the conditions of the reaction. Hydroxyanthraquinone is always discovered (after the hydrolysis of the α-sulfo acid of anthraquinone) sublimed on the walls of the reaction tube in the form of needles with a melting point 190-192°, which do not show a depression of the melting point in a mixed sample with pure α-hydroxyanthraquinone.

TABLE 1

The Influence of the Temperature on the Hydrolysis of the α-Sulfo Acid of Anthraquinone in Water (0.72 g of substance – 0.0025 mole – 25 ml of water, 6 hours)

Expt. No.	Temperature	α-Hydroxyanthraquinone obtained (%)	$K \cdot 10^3$••
1	100°	None	–
2	190	7.1•	0.2
3	210	30.7	1.02
4	230	59.63	2.52
5	250	64.3	2.87
6	300	89.3	6.21

TABLE 2

The Influence of Time on the Hydrolysis of the α-Sulfo Acid of Anthraquinone in Water (0.72 g of substance – 0.0025 mole – 25 ml of water, 230°)

Expt. No.	Time (hours)	α-Hydroxyanthraquinone obtained (%)	$K \cdot 10^3$
1	1	5.1	–
2	3	28.5	1.86
3	6	59.63	2.52
4	9	69.4	2.19
5	13	85.9	2.51

Notes: • For this experiment the time was 24 hours.

•• $K = \frac{1}{t} 2.303 \log \frac{100}{100-x}$.

• Communication XXIII, J. Gen. Chem., 25, 809 (1955) [See Consultants Bureau Translation, page 775.

The heating of the α-sulfo acid of anthraquinone in sulfuric acid of from 0.25% to 60% concentration at 230° for 6 hours, in sealed tubes, also leads to the formation of α-hydroxyanthraquinone. For sulfuric acid of concentrations from 60 to 70%, the formation of anthraquinone also begins, along with the lowering of the amount of hydroxyanthraquinone, which is formed. Finally, for 85% sulfuric acid, the sole product of the hydrolysis of the α-sulfo acid of anthraquinone is anthraquinone.

Thus, depending on the concentration of the sulfuric acid, the hydrolysis of the α-sulfo acid of anthraquinone takes place in two directions: in concentrated sulfuric acid (85%) — with the replacement of the sulfo group by hydrogen, and in dilute sulfuric acid or in water — with the replacement of the sulfo group by the hydroxyl group. Under the action of a large amount of water, at high temperatures, a special sensitivity to the OH ion of water is observed in the α-sulfo acid of anthraquinone. On the lowering of the dissociation of water, on the transition to sulfuric acid of high concentration, the catalytic role of the hydrogen ion [3] is sharply expressed, directing the reaction on the side of the ordinary course of hydrolysis, with the replacement of the sulfo group by hydrogen.

The special sensitivity of the α-sulfo acid of anthraquinone to OH ions is confirmed by the possibility of accomplishing the so-called lime fusion which is known only for the α-sulfo acid of anthraquinone, under the action of an aqueous suspension of lime, in an autoclave at 190°, with the smooth formation of α-hydroxyanthraquinone [4].

As has been pointed out above, an increase in the volume of the water promotes an increase in the speed of the hydrolysis of the α-sulfo acid of anthraquinone to α-hydroxyanthraquinone. This dilution lowers the concentration of hydrogen ions from the α-sulfo acid which is not yet hydrolyzed, and also of the sulfurous acid, which is a product of the hydrolysis of the latter. It is completely natural that the rate of the hydrolysis of the α-sulfo acid of anthraquinone increases under the influence of the hydroxyl ions from such a weak base as lime.

TABLE 3

The Influence of Sulfuric Acid on the Hydrolysis of the α-Sulfo Acid of Anthraquinone (0.72 g of substance — 0.0025 mole — 25 ml of H_2SO_4, 190°, 24 hours).

Expt. No.	Concentration of H_2SO_4 (%)	Number of moles of water per mole of α-acid	Obtained (%)	
			anthraquinone	α-hydroxyanthraquinone
1	100	4.4	None	None
2	70	193.8	13.8	10.5
3	60	327.0	13.6	10.5
4	50	388.8	None	20.2
5	40	433.0	None	16.1
6	20	508.0	None	13.4
7	10	533.0	None	13.4
8	2	551.6	None	13.6
	The same, at 230°, after 6 hours			
1	100	4.4	None	None
2	85	147.1	58.9	None
3	70	193.8	40.4	3.57
4	60	327.0	22.3	18.5
5	40	433.0	None	31.6
6	30	475.0	None	30.9
7	20	508.0	None	28.0
8	15	521.5	None	25.5
9	10	533.0	None	17.0
10	2	551.6	None	13.0
11	0.5	554.0	None	19.3
12	0.24	554.6	None	35.0
13	Water	555.0	None	59.63

The sensitivity of the α-sulfo acid of anthraquinone to the OH ion is manifested even under the conditions of heating for six hours at 100°, in a flask with a reflux condenser, in 20% sodium hydroxide (the yield of α-hydroxyanthraquinone was 3.8%).

The replacement of the sulfo group in the α-sulfo acid of anthraquinone by the hydroxyl group, both on hydrolysis in water, and in the lime fusion, is also explained by the definite influence of the carbonyl group, which leads to the very strong drawing off of electrons from the carbon atom in the α-position of the anthraquinone ring, and thus makes the replacement of the sulfo group easier [1a]. As a consequence of this property, the sulfo group of the α-sulfo acid of anthraquinone, like the sulfo group in bisulfite compounds, as is known, is very sensitive to OH ions, and is stable to H ions in aqueous solutions.

The action of water on the salts (Table 4) of the α-sulfo acid of anthraquinone is somewhat different than on the free acid. While up to 60% α-hydroxyanthraquinone was formed at 230° over a period of six hours in water, we succeeded in preparing no more than 10% of the same hydroxyanthraquinone under the

same conditions from the sodium, potassium, ammonium, and calcium salts of the α-sulfo acid. This is due to the formation of the salts of sulfurous acid instead of the free acid:

$$RSO_3Na + HOH \longrightarrow ROH + NaHSO_3.$$

It is fully possible that bisulfites and sulfites at high temperatures and pressures may turn out to have a harmful influence on the anthraquinone molecule, and thus complicate the reaction of the hydrolysis of the α-sulfo acid [7].

As is evident from Table 5, the hydrolysis of the sodium salt in dilute sulfuric acid (2% and higher) leads to a mixture of hydroxyanthraquinone and anthraquinone.

TABLE 4

The Hydrolysis of Various Salts of the α-Sulfo Acid of Anthraquinone in Water (0.762-0.775 g of the salt – 0.0025 mole – 230°, 25 ml of water, 6 hours)

Expt. No.	Salt	α-Hydroxy-anthraquinone obtained (%)
1	α-Sulfo acid	59.63
2	Na-salt	2.8
3	NH_4-salt	1.0
4	Ca-salt	9.3
5	Na-salt + 0.07 g CaO (0.0012 mole)	37.0
6	Ca-salt + 0.07 g CaO	37.0

TABLE 5

The Hydrolysis of the Sodium Salt of the α-Sulfo Acid of Anthraquinone in Sulfuric Acid (0.775 g of the salt – 0.0025 mole – 25 ml H_2SO_4, 230°, 6 hours)

Expt. No.	Concentration of H_2SO_4 (%)	Obtained (%)	
		anthraquinone	α-hydroxyanthra-quinone
1	85	83.46	None
2	70	81.07	None
3	40	15.6	11.6
4	30	9.9	12.1
5	10	1.5	4.0
6	2	0.25	2.2
7	0.5	None	15.1
8	Water	None	2.8

In order to obtain good yields of α-hydroxyanthraquinone (up to 85-90%), the sodium salt of the α-sulfo acid of anthraquinone, as the most soluble salt, should be heated with 0.5% sulfuric acid, taken in approximately stoichiometric quantities:

$$2RSO_3Na + H_2SO_4 \rightleftharpoons 2RSO_3H + Na_2SO_4,$$

at 250-300°, 18-24 hours, that is, under more rigid conditions than for the free α-sulfo acid of anthraquinone.

Having described in a previous communication the significance of mercury salts on the hydrolysis of the α-sulfo acid of anthraquinone to anthraquinone in concentrated sulfuric acid, we also studied the influence of mercury in experiments on the hydrolysis of the α-sulfo acid of anthraquinone in weak sulfuric acid and water. On the heating of the α-sulfo acid of anthraquinone in water or in sulfuric acid up to a concentration of 40%, with 1% mercuric sulfate, on the weight of the sulfo acid (or 0.25% $HgSO_4$ on the volume of the solution), the hydrolysis leads to the formation of α-hydroxyanthraquinone with the same yields as in the experiments without mercury. The heating of the α-sulfo acid of anthraquinone in water with 5% mercuric sulfate (on the weight of the sulfo acid, or 1.25% on the volume of the solution) leads to a shifting of the hydrolysis from hydroxyanthraquinone one alone to a mixture of the latter with anthraquinone (Table 6).

The heating of the α-sulfo acid of anthraquinone with 5% mercuric sulfate in sulfuric acid of a concentration of from 5-85%, leads to the formation of anthraquinone alone. The influence of the quantity of mercuric sulfate in water and in weak acids on the elimination of the phenomenon of the substitution of the hydroxyl group for the sulfo group, and on the other hand, on the development of the process of the substitution of hydrogen for the sulfo group, confirms the scheme which was indicated earlier of the action of mercury salts on the hydrolysis of the α-sulfo acid of anthraquinone. An increase in the concentration of mercury on hydrolysis in an aqueous solution of sulfuric acid, brings about an increase in the concentration of hydrated mercury salts, which, directly reacting with the sulfo acid makes this reaction the predominating one over the reaction of direct hydrolysis under the action of water alone:

a) $HOHgSO_4H + RSO_3H \longrightarrow RHgSO_4H + H_2SO_4$,

b) $RHgSO_4H + HOH \longrightarrow RH + HOHgSO_4H$.

The calculated rate constants for the reaction of the hydrolysis of the α-sulfo acid of anthraquinone for various time periods and 230° (the average value of $K \cdot 10^3 = 2.27$), indicate the monomolecular character of the process. The dependence of the rate constant of the reaction on the temperature is shown in Table 7.

TABLE 6

The Influence of Mercuric Sulfate on the Hydrolysis of the α-Sulfo Acid of Anthraquinone (0.72 g of the substance – 0.0025 mole – 230°, 6 hours)

Expt. No.	Concentration of $HgSO_4$ (%)	% of $HgSO_4$ on the sulfo acid	Obtained (%)	
			anthraquinone	α-hydroxy-anthraquinone
1	40	1	None	32.0
2	40	5	77.3	None
3	20	1	None	28.9
4	20	5	84.61	None
5	10	1	None	17.5
6	10	5	88.8	None
7	Water	1	None	59.8
8	Water	5	14.3	32.1

TABLE 7

Temperature	190°	210°	280°	250°	300°
$K \cdot 10^3$	0.2	1.02	2.52	2.87	6.21

The values for the logarithms of K, found experimentally in accordance with Arrhenius' equation [5], conform well to the line. A comparison of the rate constant for the hydrolysis of the α-sulfo acid of anthraquinone in water with the rate constants for the hydrolysis of the same acid in sulfuric acid in the presence of mercury [6], also shows that the rate of the process of the replacement of the sulfo group by hydrogen in the presence of mercury is greater than the rate of the process of the replacement of the sulfo group by the hydroxyl group.

EXPERIMENTAL

1. Starting materials: the α-sulfo acid of anthraquinone, water and sulfuric acid for the hydrolysis were prepared analogously to those described earlier.

2. The method of carrying out the hydrolysis. The hydrolysis of the α-sulfo acid of anthraquinone and its salts with water and an aqueous solution of sulfuric acid was carried out in an acid-resistant tube, 250 mm in length with a diameter of 20 mm. The heating of the tube and the working of its contents after hydrolysis was carried out analogously to the work previously described by us.

The precipitate, obtained on hydrolysis, was transferred to a funnel for filtration, washed, dried in a cabinet at 100-105°, weighed, and its melting point determined. Part of the product was crystallized from alcohol or ether. Ordinarily such crystallization, applied to products whose melting point is close to, or corresponds to, that of hydroxyanthraquinone (188-196°), leads to the formation of a pure substance, which does not show a depression of the melting point in a mixed sample with pure α-hydroxyanthraquinone. Part of the raw product, on its gentle heating on an hour glass and on a heated sand bath, easily undergoes sublimation. The presence of α-hydroxyanthraquinone was also established by the dissolution of the raw product in a 20% solution of sodium hydroxide. The product was dissolved on heating with a bluish-red coloration. On the acidification of such a solution, a greenish-yellow precipitate of α-hydroxyanthraquinone was formed.

In those cases where the obtained substance was insoluble in a sodium hydroxide solution, almost insoluble in alcohol and ether, and has a high melting point (265-272°), it was assumed to be anthraquinone. The raw product showed a reaction on the anthraquinone nucleus: coloration of zinc dust and hydrosulfite in a suspension with a sodium hydroxide solution. In this case the product was purified by sublimation or crystallization from acetic acid. The recrystallized substance melted at 276-277° and did not show a depression of the melting point in a mixed sample with pure anthraquinone.

In those cases where the obtained product is partially soluble in ether, alcohol and a sodium hydroxide solution, and has a melting point between 243 and 260°, it was assumed to be a mixture of hydroxyanthraquinone and

anthraquinone. Such a product was extracted with a 20% sodium hydroxide solution; from the latter solution raw α-hydroxyanthraquinone was isolated by acidification. The residue after extraction was washed with water, dried, weighed, and sublimed. The sublimate showed all of the characteristics of anthraquinone. The raw products of the reaction, which have a melting point between 198 and 225° are usually α-hydroxyanthraquinone containing small amounts of admixtures. They are easily purified by crystallization or sublimation. Such products were assumed to be raw α-hydroxyanthraquinone.

The precipitate, obtained on the hydrolysis of the α-sulfo acid of anthraquinone in sulfuric acid, in the presence of mercury compounds, was washed with 5% sulfuric acid, then with water, and dried. Such a product corresponds either to α-hydroxyanthraquinone, which does not contain organically linked mercury, or anthraquinone containing non-ionic mercury, or a mixture of this type of anthraquinone and α-hydroxyanthraquinone. The treatment of such products is carried out analogously to the treatment indicated above.

The balance of the products of the hydrolysis of the α-sulfo acid of anthraquinone in water (25 ml, 6 hours at 220°). 0.72 g of the α-sulfo acid of anthraquinone was taken. After hydrolysis the cooled tube was opened in 50 ml of a 0.1 N solution of NaOH. The solution was filtered from the hydroxyanthraquinone precipitate, which was carefully washed, dried, and weighed.

Obtained: 0.2570 g of hydroxyanthraquinone (46%); melting point 193°. The filtrate and the wash water were decanted in a 250 ml graduated flask. Half of the solution was back-titrated with iodine and hyposulfite.* 0.0134 g of SO_2 was found in the whole volume. To the second half of the solution was added 1 g of dry potassium chloride. The potassium salt of the α-sulfo acid of anthraquinone which was separated was filtered, washed, dried, and weighed. 0.1694 g of the salt was obtained. For the entire volume, taking into account the solubility [8], 0.3838 g of the potassium salt of the α-sulfo acid was needed, or 0.3339 g of the free sulfo acid, which constituted 46.3% of the impure acid. 0.2800 g of chloroanthraquinone was obtained from the salt which was isolated and from the mother liquor, by working with potassium chlorate [9]; this constituted 46% calculating on the original weighed portion of the α-sulfo acid. Chloroanthraquinone melted at 158° and did not show a depression of the melting point in a mixed sample with pure α-chloroanthraquinone.

In the filtrate and wash waters, after the driving off of the potassium salt, sulfuric acid was precipitated with barium chloride in the presence of ammonium chloride. 0.1022 g of $BaSO_4$ was obtained, or, calculating on the whole volume on conversion to SO_2 — 0.0556 g of SO_2. The total of the sulfurous acid obtained was: 0.0132 + 0.0556 = = 0.0688 g of SO_2, or 93.73%, calculating on the obtained hydroxyanthraquinone. The amount of sulfurous acid, oxidized to sulfuric acid, was 80.8%. Thus, at the end of the hydrolysis reaction, the concentration of sulfuric acid in the reaction mixture was established at 0.3%.

SUMMARY

1. It has been established that the α-sulfo acid of anthraquinone is capable of being hydrolyzed in water and weak sulfuric acid at 190° and higher, in a closed system, without the participation of mercury, with the replacement of the sulfo group by the hydroxyl group, forming either α-hydroxyanthraquinone, or at higher concentrations of sulfuric acid, a mixture of the latter with anthraquinone.

2. It has been established that the addition of a small amount of mercury salts to the reaction medium does not change the direction of the hydrolysis of the α-sulfo acid of anthraquinone with the replacement of the sulfo group by the hydroxyl group (formation of α-hydroxyanthraquinone); however, a larger quantity of mercury (5% of the weight of the α-sulfo acid) shifts the hydrolysis in the direction of the replacement of the sulfo group by hydrogen (formation of anthraquinone).

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[2] V. V. Kozlov and A. A. Egorova.

[3] A. A. Spryskov, J. Gen. Chem., 8, 1857 (1938).

* 2.09 ml 0.1 N hyposulfite was used.
** See C. B. Translation, p. 535.
*** See C.B. Translation, p. 775.

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THE ACTION OF ETHYLENE OXIDE ON α-AMINOPYRIDINE AND ON N-ALKYL-α-PYRIDONEIMINES

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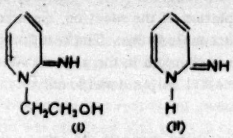
In the process of the study of the precipitability of compounds of the pyridine series with carbonic acid, one of us and M. S. Kondakova established [1] that a compound of the α-aminopyridine type is not precipitated from its solution in moist ether. This fact served Ya. L. Goldfarb, O. N. Setkina and Ya. L. Danyushevsky as the basis for the conclusion [2] that α-aminopyridine does not possess the properties of a tautomeric substance, at least in a degree sufficient for its discovery in its chemical transformations. The results of the study of the ultra-violet adsorption spectra of this amine in various solvents also did not agree with the idea of its tautomerism, since the bands characteristic for the α-pyridoneimine forms [3, 6] are not observed.

Assuming that α-aminopyridine reacts only in the amine form, it is also possible to explain its conversions which are ordinarily considered a result of the influence of the pyridoneimine form (II). The difficulties, which at first glance appear insurmountable, arise only in the interpretation of the reaction with ethylene oxide. As I. L. Knunyants [4] showed, the reaction product in this case is N-(β-hydroxyethyl)-α-pyridoneimine (I); without the participation of a third component, the latter may be formed only from the second tautomeric form (II).

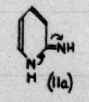


However, on more careful examination of the question, it is evident that the possibility of the formation of compound (I) is not necessarily associated with the presence of a hydrogen atom at the ring nitrogen atom: as is known, ethylene oxide easily reacts not only with primary and secondary, but also with tertiary amines. In the latter case, of course, a third component capable of giving up a proton, such as water, alcohol, etc., must participate in the reaction.

Thus, only in that case could it be confirmed that α-aminopyridine reacts with ethylene oxide in the pyridonimine form, if it were certain that the reaction would take place also in the absence of a compound having such an ability.

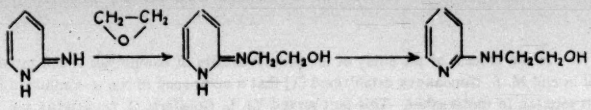
In order to clarify this side of the question, we studied the relationship of α-aminopyridine to ethylene oxide in anhydrous dioxan, which, as is known, does not possess the property of being a proton donor, and in aqueous dioxan. The experiments were carried out under the same conditions – the solutions were allowed to stand for three to five days at room temperature, and then the ethylene oxide and the solvent which had not entered into the reaction were driven off and the residue was vacuum distilled. Thereupon, the role of the water was fully explained: in the experiments with anhydrous dioxan almost all of the aminopyridine was recovered in an unchanged form, while in the parallel experiments with water, 25% (calculated on the amine taken) of N-(β-hydroxyethyl)-α-pyridoneimine was obtained. This relationship was maintained on the replacement of dioxan with acetone, with the sole difference that in the dry acetone only a very small quantity of base (I) was formed.

If along with these observations, we turn out attention to the data [5] relating to the role of water in the reactions of ethylene oxide with primary and secondary amines, it becomes evident that the fact of the formation of N-(β-hydroxyethyl)-α-pyridoneimine in general may not serve as an indicator of the participation of one or another tautomeric form of α-aminopyridine in the reaction. However, starting from other premises, it is possible to come to the conclusion that the aminopyridine, and not the α-pyridoneimine form reacts with ethylene oxide: this is contrary to the view of I. L. Knunyants [4]. Here the most important fact is, as was pointed out above, the circumstance that the second of these forms was not detected either chemically (through the use of carbonic acid), nor spectrographically. In addition, since ethylene oxide ordinarily reacts as an electrophylic agent, it is possible to assume that its action must first of all be directed to that nitrogen atom where, under the influence of the attacking agent, the electron density increases. It is easy to see that, in a molecule of type (II), the accumulation of electron density may take place (in the process of interaction) only in the direction shown by the arrows (IIa).

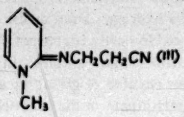


(IIa)

The correctness of this point of view is confirmed by the data of investigations [1, 2, 6, 11, 17] relative to the basicity of the nitrogen atoms in such systems. Thus, if ethylene oxide would react with form (II), the main reaction product would be not N-(β-hydroxyethyl)-α-pyridoneimine (I), but its isomer:



This idea of the reaction of ethylene oxide with compounds of the α-pyridoneimine type needed experimental confirmation, since in the work cited above [4] there are indications which amount to the idea that the imino group of base (I) is incapable of adding the oxide. If this indication were to correspond to the actual relationship, the imino group of the N-alkyl-α-pyridoneimines would have to have special properties ascribed to it, since according to the published data [7], the kinetics of the reaction of ethylene oxide with amines is not associated with any dependence upon their structure. In this connection, it was desirable first to verify whether or not bases of the indicated type were capable of other transformations which are characteristic for compounds with an NH group, for example, the addition of ethyl cyanide or alkylation under the conditions of reducing alkylation.

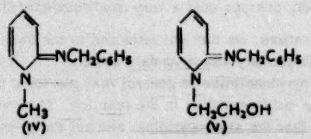


(III)

For this purpose we studied the action of acrylonitrile, and on the other hand a mixture of benzaldehyde and formic acid on the simplest representative of the N-alkyl- or pyridoneimines – N-methyl-α-pyridoneimine. Even the first experiment showed that this base easily enters into interaction with acrylonitrile. The reaction evidently goes in the cold, since on the mixing of the reagents (1:1) a warming up of the reaction mixture was observed; for the completion of the reaction, the mixture was heated for some time over a water bath in a sealed tube. The reaction product is a substance with a low melting point which is changed in the air, and which corresponds in its composition to the expected N-methyl-α-pyridone(β-ethyl cyanide)-imine (III).

The fact of its formation from N-methyl-α-pyridoneimine indicates that the imino group of the latter conducts itself in a "normal" way in relation to acrylonitrile; this circumstance acquires still greater interest on comparison with the observation that acrylonitrile does not react with α-aminopyridine [8].

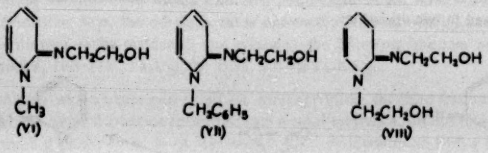
On the action on N-methyl-α-pyridoneimine of a mixture of benzaldehyde and formic acid, under the conditions described by A. E. Chichibabin and I. L. Knunyants [9], for the addition of the benzyl group to α-aminopyridine, N-methyl-α-pyridone-benzylimine (IV) which was described previously by Ya. L. Danyushevsky and Ya. L. Goldfarb [10], was formed. The indicated mixture reacts in an analogous manner with N-(β-hydroxyethyl)-α-pyridoneimine (I), forming N-(β-hydroxyethyl)-α-pyridone-benzylimine (V), the structure of which, as a product of the replacement of hydrogen in the imino group of base (I) is confirmed by the fact that this same compound (V) is obtained by the action of benzyl iodide on compound (I).



(IV) (V)

Since it follows from the above-described observations that the imino group of N-alkyl-α-pyridoneimines have properties inherent in compounds with such functions, one could expect that in spite of the point of view expressed earlier on this point [4], bases of this type will add ethylene oxide. This hypothesis was confirmed by experiment. Specifically, by the action of ethylene oxide on the corresponding alkyl-pyridoneimines, we obtained

N-methyl-α-pyridone-(β-hydroxyethyl)-imine (VI), N-benzyl-α-pyridone-(β-hydroxyethyl)-imine (VII) and N-(β-hydroxyethyl)-α-pyridone-(β-hydroxyethyl)-imine (VIII).

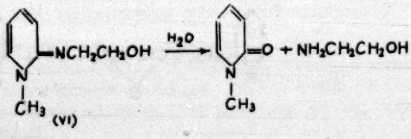


The last of the enumerated bases was also isolated by us from a mixture which was obtained by the action of ethylene oxide on α-aminopyridine (see below).

Base (VII), which was formed under the conditions described below from the N-benzyl-α-pyridoneimine was not fully separated from the latter by distillation. In general, the separation of the hydroxyethyl derivatives of this series is associated with considerable difficulties, and requires various methods. This is associated with the fact that on the action of ethylene oxide on N-alkyl-α-pyridoneimine, a great deal of tar is always obtained, and that on vacuum distillation it is not possible to separate fractions boiling in a very narrow interval; therefore, in order to separate N-benzyl-α-pyridone-(β-hydroxyethyl)-imine (VII), we had to resort to the repeated recrystallization of the salt. By this method its hydrochloride was isolated, from which, by treatment with potash, the free base was obtained with a yield of 37%, calculated on the original N-benzyl-α-pyridonimine.

The same method was used for the separation of the compound associated with base (VI); a constant melting point of the hydrochloride was achieved only after a number of recrystallizations. The yield of the base did not rise above 25%.

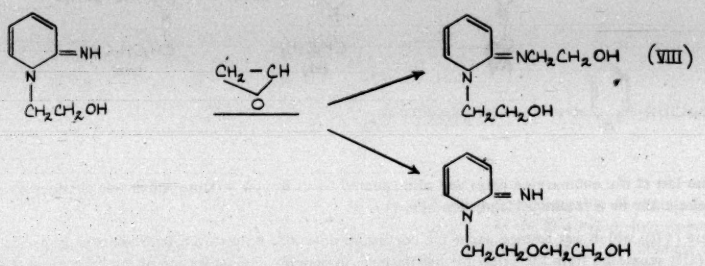
The influence of water on the reaction of the addition of hydroxyethyl to N-alkyl-α-pyridoneimines was established on the example of N-methyl-α-pyridoneimine. The experiments, as in the case of α-aminopyridine, were carried out in parallel. Dioxan was used as a solvent. In the experiment without water, the N-methyl-α-pyridoneimine was recovered unchanged; in the experiment with water, N-methyl-α-pyridone-(β-hydroxyethyl)-imine was obtained with a yield of 20%. The latter compound (VI) forms, on heating with an alkaline solution, similar to other bases of this type, the corresponding pyridone and amine:



The separation of the products of hydrolysis was carried out through the use of carbonic acid, which precipitates ethanolamine from an ether solution, but does not precipitate N-methyl-α-pyridone [11].

Since the experiments showed that N-alkyl-α-piridoneimine is capable of entering into interaction with ethylene oxide, it may be assumed that, in the mixture which is formed on the interaction of α-aminopyridine with an excess of ethylene oxide, there is present the product of the addition of two molecules of the latter structure (VIII). On the distillation of such a mixture (a mixture was taken from the experiments with aqueous acetone) a reddish oil, boiling over a wide interval, was obtained, from which, by further working, we succeeded in separating in the form of its hydrochloride, a compound which actually corresponded in its composition to formula (VIII). The base, separated from this salt, proved to be a yellow crystalline substance, which deliquesced in the air and which absorbed carbonic acid; it is also formed, but with smaller yields (9-12%), by the action of ethylene oxide in a water-acetone or alcohol solution on N-(β-hydroxyethyl)-pyridoneimine (I).

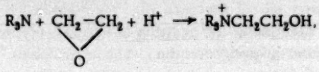
Although this compound corresponded in its composition to the product of the addition of two molecules of ethylene oxide to a molecule of α-aminopyridine, the question of its structure remained undecided, since according to formal considerations, the process of the addition of ethylene oxide to N-(β-hydroxyethyl)-α-pyridoneimine may be imagined in two directions.



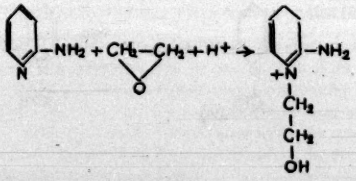
(VIII)

It proved to be possible to make a choice between these two structures on the basis of a study of the hydrolysis of this compound: the products of hydrolysis proved to be N-(β-hydroxyethyl)-α-pyridone and ethanolamine, which corresponds to formula (VIII).

We saw above that ethylene oxide reacts with α-aminopyridine under the same conditions as with other amines. Thus, on the consideration of the question of the mechanism of this process, it is possible to be attracted to the earlier growth of the idea of the reaction of ethoxides with amines [5, 12]. In the most general form, this reaction may be represented by the scheme [7]



and for aminopyridine, if as indicated above, we assume that the amine form reacts, the reaction may be represented by the following scheme:



Here, in essence, is illustrated the property of the oxide, which was noted by Brönsted and Kilpatrick [13], to enter into interaction only upon its simultaneous attack by an acid and a base. This idea, requiring the participation in the reaction with amines of substances capable of giving up a proton, is not in agreement with the data of some investigators, particularly K. D. Petrov and G. V. Talkovsky [14], who showed that at 70-100° ethylene oxide is added to aniline without the addition of water. It seems to us, however, that facts of this kind do not contradict the point of view which has been presented on the mechanism of the reaction of ethylene oxide with amines, since it is not excluded that under certain conditions the function of a proton donor is taken upon itself by a second amine molecule (aniline), which is reacting with the oxide.

EXPERIMENTAL

1. The action of ethylene oxide* on α-aminopyridine** in methyl alcohol. A solution of 26.7 g of α-aminopyridine in 15 ml of anhydrous methanol was mixed with 13 g of ethylene oxide. The mixture was allowed to stand at room temperature. After four days, the ethylene oxide and methyl alcohol which had not reacted were distilled off. On vacuum distillation of the residue (7 mm pressure), the following fractions were collected: the first, 82-105°, 11.1 g; the second, 106-170°, 16.1 g; the third, 171-193°, 5.6 g.

The first fraction was a mixture which contained chiefly α-aminopyridine; the third fraction was a mixture of a red oil and yellow crystals; the second fraction solidified into a solid substance, on the recrystallization of which (from alcohol) was obtained 8 g (20%)*** of N-(β-hydroxyethyl)-α-pyridoneimine with a melting point of 127-128°. According to the literature data [4], the melting point of this compound is 112-113°.

Found %: C 60.78, 60.50; H 7.26, 7.20. $C_7H_{10}ON_2$. Calculated %: C 60.86; H 7.24.

The hydrochloride is a hygroscopic, colorless, rhombic crystalline substance with a melting point of 146-147.5° (from alcohol).

Found %: C 48.47, 48.43; H 6.32, 6.44; N 16.32, 16.30. $C_7H_{11}ON_2Cl$. Calculated %: C 48.13; H 6.30; N 16.04.

2. The action of ethylene oxide on α-aminopyridine in dry dioxan. A solution of 8.7 g of α-aminopyridine in 7 ml of dioxan was mixed with 4.6 g of ethylene oxide. The mixture was allowed to stand at room temperature for two and one half days. The unreacted ethylene oxide and dioxan were distilled off. On the distillation of the residue in a vacuum, 7.6 g of the original α-aminopyridine was obtained.

3. The action of ethylene oxide on α-aminopyridine in dioxan in the presence of water. A solution of 10.4 g of α-aminopyridine in 8 ml of dioxan was mixed with 2 ml of water and 5.4 g of ethylene oxide. The mixture was allowed to stand at room temperature for 2.5 days. Then the unreacted ethylene oxide and dioxan were distilled off. On the distillation of the residue in a vacuum, the following fractions were obtained: the first, 85-166° (7 mm), 6.9 g; the second, 143-165° (2-3 mm), 4.2 g.

The first fraction was a clear liquid which quickly began to crystallize, consisting mainly of the original α-aminopyridine; from the second fraction was obtained, after recrystallization from alcohol, 3.4 g (25%) of N-(β-hydroxyethyl)-α-pyridoneimine with a melting point of 127.5°. On the melting of its mixture with a known sample of N-(β-hydroxyethyl)-α-pyridoneimine, a depression of the melting point was not observed.

4. The action of ethylene oxide on α-aminopyridine in acetone without water. The experiments in acetone were carried out just as the experiments in dioxan were. From 20.6 g of α-aminopyridine, 18.4 g was recovered unchanged. In addition, 0.3 g of N-(β-hydroxyethyl)-α-pyridoneimine was separated.

5. The action of ethylene oxide on α-aminopyridine in acetone in the presence of water. From 20 g of α-aminopyridine was obtained 5.9 g of N-(β-hydroxyethyl)-α-pyridoneimine and 9.9 g of a high-boiling, dark red, thick liquid; 5.8 g of α-aminopyridine was recovered unchanged. The high-boiling fractions, obtained in analogous experiments, were combined and worked separately. From them (item 15) N-(β-hydroxyethyl)-α-pyridone-(β-hydroxyethyl)-imine was isolated.

6. The action of acrylonitrile on N-methyl-α-pyridoneimine. 5.5 g of N-methyl-α-pyridoneimine [15] was mixed in a thick-walled tube with 2.7 g of acrylonitrile. The mixture was heated for five minutes. After this, as the reaction mixture reached room temperature, the tube was sealed and heated over a boiling water bath for three hours. On the opening of the tube, no pressure was detected. The thick liquid which was obtained was vacuum distilled (9 mm): first fraction, 100-168°, 1.9 g (the main part went over at 100°); the second fraction, 169-170°, 3.7 g.

The first fraction, judging by its boiling point, was mainly the original N-methyl-α-pyridoneimine; the second fraction was a yellow liquid which began to crystallize almost immediately. The analysis was carried out immediately after distillation.

* For this and the subsequent experiments, we took ethylene oxide which had been freed of acetaldehyde and dried by passing through a column containing solid potassium hydroxide.

** The α-aminopyridine needed for the experiment was purified by means of dissolving the technical products in benzene, the distillation of the benzene after absorbing the traces of moisture, and the vacuum distillation of the residue.

*** Here and below, the yield is given in % of the theoretical, calculated on the original base.

Found %: C 67.33, 67.31; H 6.84, 6.79; N 26.10, 26.01. $C_9H_{11}N_3$. Calculated %: C 67.08; H 6.83; N 26.08.

N-Methyl-α-pyridine-(β-ethyl cyanide)-imine quickly changed in the air; the substance absorbs carbonic acid and is hygroscopic.

7. The interaction of N-methyl-α-pyridoneimine with benzaldehyde in the presence of formic acid. To 9.8 g of benzaldehyde was added 10 g of N-methyl-α-pyridoneimine, and then 21.2 g of anhydrous formic acid. The mixture was heated for six hours — at first at 150°, and toward the end at 170° — after which it was worked with an excess of hydrochloric acid. The unreacted benzaldehyde and formic acid were extracted with ether. The acid solution was alkalized with a 50% potassium hydroxide solution, and then saturated with solid alkali. The oil which came to the surface was extracted with hot benzene. From the extract the benzene was distilled off, and the precipitate subjected to fractional distillation: in the first fraction, 106-112° (15-16 mm), 6.4 g; the second fraction 194-195° (15 mm), 4.4 g.

The first fraction was the original substance; the second fraction was N-methyl-α-pyridonebenzylimine. The melting point of the picrate was 123.5°. On the melting of a sample of this picrate with the picrate of N-methyl-α-pyridonebenzylimine [10] a depression of the melting point was not observed.

8. The action of benzaldehyde on N-(β-hydroxyethyl)-α-pyridoneimine in the presence of formic acid. To 10 g of N-(β-hydroxyethyl)-α-pyridoneimine was added 7.7 g of benzaldehyde and 16.6 g of anhydrous formic acid. The mixture was heated until the cessation of the intensive evolution of carbonic acid (20 hours). The oil which was obtained after the corresponding treatment (as in item 7) was extracted with ether. The ether was distilled off. The residue was a thick liquid, mixed with a small amount of crystals. The crystals were separated, washed with ether, and recrystallized from alcohol. 0.4 g of a substance with a melting point of 127-128° was separated. A mixture of this substance with N-(β-hydroxyethyl)-α-pyridoneimine melted at the same temperature.

On the distillation of the filtrate, 7.7 g of an oil with a melting point of 176-210° (4 mm) was obtained. It was dissolved in 50 mg of benzene. The benzene solution was extracted with water in order to drive off the unreacted N-(β-hydroxyethyl)-α-pyridoneimine. The residue, after driving off of the benzene, was distilled. At 191-193° (2 mm), 5.5 g (33%) of a yellow oil went over; it was N-(β-hydroxyethyl)-α-pyridonebenzylimine.

Found %: C 73.53, 73.93; H 7.19, 7.12; N 12.46, 12.26. $C_{14}H_{16}ON_2$. Calculated %: C 73.68; H 7.01; N 12.28.

Its picrate melted at 115-115.5° (from alcohol).

Found %: N 15.36, 15.26. $C_{20}H_{19}O_8N_5$. Calculated %: N 15.31.

9. The action of benzyl iodide on N-(β-hydroxyethyl)-α-pyridoneimine. A solution of 4.4 g of N-(β-hydroxyethyl)-α-pyridoneimine in 4 ml of alcohol was mixed with a solution of 7.7 g of benzyl iodide in 40 ml of alcohol. The reaction mixture was allowed to stand at room temperature, then the alcohol was distilled off. The residue was washed with benzene and dissolved in hydrochloric acid; a tar was separated from the acid solution and the solution was evaporated over a water bath. The remaining viscous liquid was dissolved in water. The aqueous solution was saturated with potash. The yellow oil which came to the surface was extracted with benzene. The benzene solution was washed with water; the original base went into the water layer. The oil which remained after the benzene was driven off was distilled. At 197-199° (3 mm), 2.2 g (30%) of a thick, yellow liquid went over; the picrate of this liquid was identified (mixed sample) with the picrate of N-(β-hydroxyethyl)-α-pyridonebenzylimine, obtained by the action of benzaldehyde and formic acid on N-(β-hydroxyethyl)-α-pyridoneimine.

10. The action of ethylene oxide on N-benzyl-α-pyridoneimine. To a solution of 25.9 g of N-benzyl-α-pyridoneimine [15] in 25 ml of methyl alcohol was added 14 g of ethylene oxide. The mixture was allowed to stand at room temperature for several days, then the unreacted ethylene oxide and methyl alcohol were distilled off. The residue was subjected to fractional distillation.

The fraction, boiling at 187-196° (2 mm), was dissolved in an excess of dilute (1:1) hydrochloric acid, and the solution was evaporated until dry.

The crystalline mass which remained was recrystallized from alcohol. 15 g of the hydrochloride of N-benzyl-α-pyridone-(β-hydroxyethyl)-imine with a melting point of 169-172° was obtained.

Found %: C 63.89, 63.92; H 6.55, 6.53. $C_{14}H_{17}ON_2Cl$. Calculated %: C 63.51; H 6.42.

7 g of this salt was converted into the base: to a saturated solution of the salt in water, potash was added carefully with agitation. The oil which came to the surface was dissolved in benzene. The benzene was distilled off. On the distillation of the residue, 5.9 g of N-benzyl-α-pyridone-(β-hydroxyethyl)-imine with a boiling point of 171.5-172.5° at 2 mm was obtained.

Found %: C 73.64, 73.36; H 6.96, 7.18; N 12.33, 12.06. $C_{14}H_{16}ON_2$. Calculated %: C 73.68; H 7.01; N 12.28.

N-Benzyl-α-pyridone-(β-hydroxyethyl)-imine is a yellow, thick oil, which is quite soluble in benzene, ether and difficultly soluble in water. In the air it darkens.

11. The action of ethylene oxide on N-methyl-α-pyridoneimine. In a thick-walled flask was mixed a solution of 12.1 g of N-methyl-α-pyridoneimine in 7 ml, and 15.1 g of ethylene oxide in 5 ml of anhydrous methyl alcohol. The reaction mixture was allowed to stand at room temperature for 4 days, then the unreacted ethylene oxide and methyl alcohol were distilled off. The residue was vacuum distilled. The fraction with a boiling point of 140-147° (7 mm), was a thick, yellow liquid which did not crystallize on cooling. From it was obtained 6.0 g of the hydrochloride of N-methyl-α-pyridone-(β-hydroxyethyl)-imine in the form of white, shining needles with a melting point of 147-149° (from alcohol).

Found %: C 51.17, 51.31; H 7.01, 6.98; Cl 19.16, 19.23. $C_8H_{13}ON_2Cl$. Calculated %: C 50.92; H 6.89; Cl 18.83.

A solution of 5.3 g of the hydrochloride in 10 ml of water was saturated with potash. The thick, yellow oil which rose to the surface was shaken up many times with small portions of hot benzene. From the extract, the benzene was distilled off. The residue was distilled. At 145.5-146.5° (7 mm), a yellow, very thick oil, went over.

Found %: C 63.23, 62.93; H 8.12, 8.01. $C_8H_{12}ON_2$. Calculated %: C 63.15; H 7.89.

The yield of N-methyl-α-pyridone-(β-hydroxyethyl)-imine was 4.2 g (25%). The picrate was in the form of crystals with a melting point of 115-116° (from alcohol).

Found %: N 18.60, 18.35. $C_{14}H_{15}O_8N_5$. Calculated %: N 18.37.

12. The action of ethylene oxide on N-methyl-α-pyridoneimine in dry dioxan. A solution of 18.7 g of carefully dried N-methyl-α-pyridoneimine in 15 ml of dioxan, was mixed with 15.2 g of ethylene oxide. The mixture was allowed to stand at room temperature for three days. The unreacted ethylene and dioxan were driven off from the reaction mixture. The liquid which remained (18.6 g) was distilled. At 97-98° (9 mm), 17.8 g of N-methyl-α-pyridoneimine went over.

13. The action of ethylene oxide on N-methyl-α-pyridoneimine in dioxan in the presence of water. A solution of 18.8 g of N-methyl-α-pyridoneimine in 15 ml of dioxan mixed with 3.1 ml of water and 15.3 g of ethylene oxide. The mixture was allowed to stand for three days. The unreacted ethylene and dioxane were distilled off from the reaction mixture. The residue (20.5 g) was distilled.

From the fraction with a boiling point of 157-157.5° at 10 mm (4.9 g), was obtained a picrate with a melting point of 115-116°. Its mixture with the picrate of N-methyl-α-pyridone-(β-hydroxyethyl)-imine melted without giving a depression of the melting point.

14. The hydrolysis of N-methyl-α-pyridone-(β-hydroxyethyl)-imine. 1.2 g of N-methyl-α-pyridone-(β-hydroxyethyl)-imine was mixed with 7 ml of a 25% solution of sodium hydroxide and 10 ml of water. The solution was boiled for four hours. After cooling, the liquid was saturated with solid sodium hydroxide. The oil which rose to the surface was dissolved in a large amount of ether, and carbonic acid was passed through the filtered ether solution. The ether solution was decanted with the oil which was precipitated – the carbonate. The ether was distilled off; in the residue was a thick, colorless liquid. From this substance was obtained a picrate with a melting point of 141.5-142.5°; the picrate of N-methyl-α-pyridone, according to the data of Chichibabin and Konovalova [16] melts at 140-141°. A mixture of the obtained substance with the picrate of N-methyl-α-pyridone melted at the same temperature.

From the carbonate also a picrate was obtained with a melting point of 157-158°. A mixture of it with the picrate of ethanolamine melted without giving a depression of the freezing point.

15. The separation of N-(β-hydroxyethyl)-α-pyridone-(β-hydroxyethyl)-imine from the high-boiling fraction, obtained in the experiments on the action of ethylene oxide on α-aminopyridine in the presence of water. In the experiment was taken 13 g of the red, high-boiling oil, which was obtained on the distillation of the mix-

tures from the experiments on the interaction of α-aminopyridine with ethylene oxide. The oil was dissolved in 1 liter of boiling benzene. The crystals, which settled out on cooling of the solution, were separated (1 g); their melting point was 127-128°, which corresponds to the melting point of N-(β-hydroxyethyl)-α-pyridoneimine. The benzene was distilled off from the mother liquor. The residue was distilled. The fraction with a boiling point of 167-187° at 2 mm (8.6 g) was a thick liquid; it was dissolved in dilute (1:1) hydrochloric acid. After several recrystallizations, 4.3 g of a substance with a melting point of 123-124.5° was obtained.

Found %: C 49.81, 49.49; H 6.83, 6.54; N 12.74, 12.67; Cl 16.56, 16.59. $C_9H_{15}O_2N_2Cl$. Calculated %: C 49.42; H 6.86; N 12.81; Cl 16.24.

The salt which was separated was the hydrochloride of N-(β-hydroxyethyl)-α-pyridone-(β-hydroxyethyl)-imine; it is a white, hygroscopic crystalline substance, which is quite soluble in alcohol. 1 g of the base with a melting point of 71-72° (from alcohol) was obtained from 1.5 g of the salt.

Found %: C 59.26, 59.10; H 7.83, 7.72; N 15.29, 15.39. $C_9H_{14}O_2N_2$. Calculated %: C 59.34; H 7.69; N 15.38.

N-(β-Hydroxyethyl)-α-pyridone-(β-hydroxethyl)-imine is a yellow crystalline substance, which is quite soluble in alcohol, less so in benzene, ether, and ethyl acetate, and very difficultly soluble in heptane. Its picrate melts at 119-120.5° (from alcohol).

Found %: N 17.22, 17.07. $C_{15}H_{17}O_9N_5$. Calculated %: N 17.03.

16. The action of ethylene oxide on N-(β-hydroxyethyl)-α-pyridoneimine in acetone in the presence of water. A solution of 3.6 g of N-(β-hydroxyethyl)-α-pyridoneimine in 20 ml of acetone was mixed with 4 ml of water and 1.5 ml of ethylene oxide. The mixture was allowed to stand for one month, then the acetone and the unreacted ethylene oxide were distilled off. The thick mass which remained was dissolved in boiling benzene. The undissolved part (tar) was thrown away. On cooling, an oil precipitated from the solution; the oil was separated from the benzene solution and dissolved in a new portion of benzene. Part of the oil again was not dissolved. The black oil which was precipitated on the cooling of the solution was not treated further. The benzene solutions were combined, and the solvent was distilled off. On distillation of the residue at 170-182° (2-3 mm) an oil went over; it was dissolved in dilute (1:1) hydrochloric acid. The acid solution was evaporated. The thick liquid which remained after standing over sulfuric acid, was worked with hot ethyl alcohol. 0.7 g of a substance which, after drying over sulfuric acid had a melting point of 123.5°, was isolated. A mixed sample of the obtained substance with the hydrochloride of N-(β-hydroxyethyl)-α-pyridone-(β-hydroxyethyl)imine did not give a depression of the melting point.

17. The hydrolysis of N-(β hydroxyethyl)-α-pyridone-(β-hydroxyethyl)-imine. a) N-(β-Hydroxyethyl)-α-pyridone-(β-hydroxyethyl)-imine (1.4 g) was dissolved in 18 ml of a 16% solution of sodium hydroxide. After boiling for eight hours, the solution was saturated with sodium hydroxide and extracted with ether; the ether solution was saturated with carbonic acid. The oil which was precipitated — the carbonate — was dissolved in alcohol. The picrate with a melting point of 157-158° was obtained from the alcohol solution. The mixture of this substance with the picrate of ethanolamine did not give a depression of the melting point.

b) The hydrochloride of N-(β-hydroxyethyl)-α-pyridone-(β-hydroxyethyl)-imine (1 g) was dissolved in 5 ml of a 10% solution of potassium hydroxide. After boiling for four hours (ammonia was not separated in this case), the solution was cooled, saturated with carbon dioxide, and evaporated. The white, solid mass which was obtained was ground into powder, which was then dried in a vacuum at 100°. It was shaken up several times with chloroform. The obtained solution was filtered, and the solvent was distilled off. The residue was recrystallized from benzene. The substance precipitated in the form of thin, long, colorless needles. The crystals were separated, washed with benzene, petroleum ether, and dried in a vacuum over paraffin; their melting point was 94°, their weight 0.45 g (71.4%). The mixture of this substance with N-(β-hydroxyethyl)-α-pyridone, obtained by the saponification of N-(β-hydroxyethyl)-α-pyridoneimine, melted at the same temperature.

SUMMARY

1. It has been shown that in correspondence with previously known data on the reaction of amines with ethylene oxide, the latter reacts with α-aminopyridine only in the presence of water or alcohol.

2. It has been shown that N-alkyl-α-pyridoneimine with an unsubstituted imino group reacts with ethylene oxide with the formation of the corresponding β-hydroxyethyl derivatives. It has been established that the reaction takes place only in the presence of water or alcohol.

3. It has been established that on the reaction of ethylene oxide with α-aminopyridine, along with N-(β-hydroxyethyl)-α-pyridoneimine, which has been described in the literature, there is also formed the dihydroxyethyl derivative – N-(β-hydroxyethyl)-α-pyridone-(β-hydroxyethyl)-iimine.

4. It has been shown that N-alkyl-α-pyridoneimine enters into a reaction of the reduction aralkylization and a reaction of the addition of ethyl cyanide.

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* See Consultants Bureau Translation, page 129.

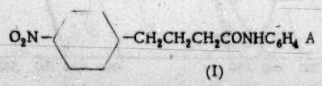
** See Consultants Bureau Translation, page 137.

*** See Consultants Bureau Translation, page 1283.

XXVIII. A COMPARATIVE STUDY OF THE ABSORPTION SPECTRA OF THE ARYLAMINES OF p-NITROPHENYLACETIC, p-NITROHYDROCINNAMIC, γ-(p-NITROPHENYL)-BUTYRIC AND p-NITROBENZOIC ACIDS

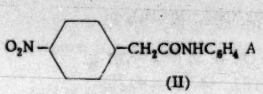
E. A. Smirnov

In our preceding communication [1], we examined the phenomena of color in the arylamines of γ-(p-nitrophenyl)-butyric acid, corresponding to formula (I), where A equals OCH_3, OH, $N(CH_3)_2$ in the meta- or para-position in relation to the NH group:

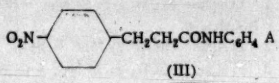


(I)

It was established that these compounds, in their coloration, are closely analogous to the derivatives of p-nitrophenylacetic (II) and p-nitrohydrocinnamic (III) acids, which have been described previously [2].



(II)



(III)

But, if, on the transition from the derivatives of p-nitrophenylacetic acid to the derivatives of p-nitrohydrocinnamic, a certain lessening of the coloration is observed, on the transition from the latter to the derivatives of γ-[p-nitrophenyl]-butyric acid, a heightening of the coloration is observed. This regularity, which is manifested both in compounds containing the $N(CH_3)_2$ group in the position of A in the formula, and in the hydroxy derivatives, was established by us on the basis of visual observations and was confirmed by the examination of the spectra corresponding to them.

In the present work the absorption spectra of the above-indicated three series of compounds are examined, the absorption spectra of the corresponding p-nitrobenzoyl derivatives being taken also for comparison.

The absorption spectra of homologous compounds, containing two chromophores, separated by means of one, two or three CH_2 groups, have been studied in detail by Ramart-Lucas [3]. According to these investigations, compounds with two and three CH_2 groups in connecting links, "have practically the same absorption" this absorption coinciding with the sum of the "limiting" absorptions of the separate chromophores. However, in the indicated investigations, it is a question of chromophores which do not have clearly expressed opposite polarity, and thus, the influence of the latter on the absorption of light was not examined.

The phenomena of coloration in nitrobenzene derivatives of aromatic amines and their absorption spectra were described in detail by V. A. Izmailsky and E. A. Smirnov [4]. The curves given by the authors have, however, a qualitative character (they were obtained by the Baily method). In order to have more comparable data, we carried out quantitative measurements of the same compounds for the present investigation; on the basis of these data, we have plotted the corresponding absorption curves.

As is evident from Figs. 1, 2, 3 and 10, 11, and 12, the absorption curves of the analogous derivatives of the first three series of compounds are very close to each other and at the same time, are quite different from the absorption curves of the p-nitrobenzoyl derivatives. Thus, with the presence of an electron donor group in the para-position in relation to the NH group, the absorption curves of the first three series of compounds are characterized by one clearly-expressed short-wave maximum, which lies in the region of 254-260 mμ in compounds with an OCH_3 group, 258-260 mμ in compounds with an OH group, and 274-278 mμ in compounds with an $N(CH_3)_2$ group, and by only a very weakly expressed maximum in the region of approximately 340 mμ. In the

corresponding p-nitrobenzoyl derivatives there are two clearly-expressed maxima: the first (short-wave), lying in the region of 250-256 mμ for compounds with a OCH_3 group, 252-254 mμ for compounds with an OH group, and at 270 mμ for compounds with an $N(CH_3)_2$ group; the second (long-wave) lying at 326-327 mμ for compounds with a p-OCH_3 group, 333-336 mμ for compounds with a p-OH group and 380 mμ for p-$N(CH_3)_2$ derivatives.

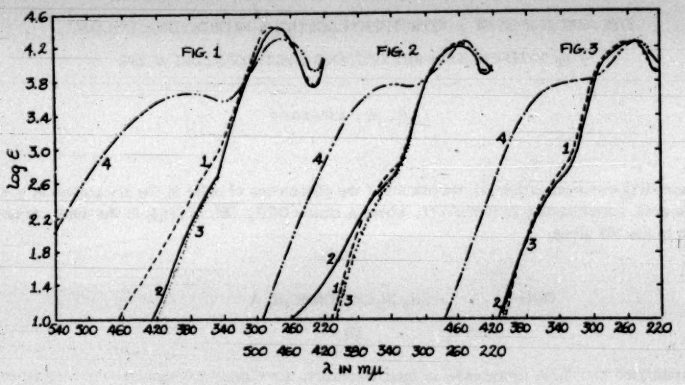


Fig. 1. 1) Npha – $N(CH_3)_2$-p; 2) Nhc – $N(CH_3)_2$-p; 3) Nphb – $N(CH_3)_2$-p; 4) Nbz – $N(CH_3)_2$-p.

Fig. 2. 1) Npha – OH-p; 2) Nhc – OH-p; 3) Nphb – OH-p; 4) Nbz – OH-p.

Fig. 3. 1) Npha – OCH_3-p; 2) Nhc – OCH_3-p; 3) Nphb – OCH_3-p; 4) Nbz – OCH_3-p.

Npha = p-$O_2NC_6H_4CH_2CONHC_6H_4$; Nhc = p-$O_2NC_6H_4CH_2CH_2CONHC_6H_4$; Nphb = p-$O_2NC_6H_4CH_2CH_2CONHC_6H_4$ Nbz = p-$O_2NC_6H_4CONHC_6H_4$.

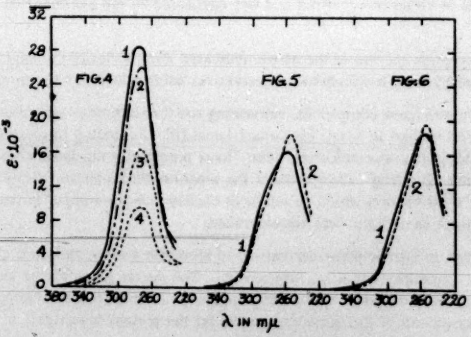


Fig. 4. 1) p-$O_2NC_6H_4CH_2CH_2CONHC_6H_4N(CH_3)_2$-p; 2) represents the sum of the absorption of 3 and 4; 3) p-$CH_3CONHC_6H_4N(CH_3)_2$; 4) p-$O_2NC_6H_4CH_3$.

Fig. 5. 1) p-$O_2NC_6H_4CH_2CH_2CONHC_6H_4NOH$-p; 2) represents the sum of absorption of p-$O_2NC_6H_4CH_3$ and p-$CH_3CONHC_6H_4OH$.

Fig. 6. 1) p-$O_2NC_6H_4CH_2CH_2CONHC_6H_4OCH_3$-p; 2) represents the sum of absorption of p-$O_2NC_6H_4CH_3$ and p-$CH_3CONHC_6H_4OCH_3$.

The position of the short-wave maximum depends first of all on the character of the electron donor group: on the presence of an $N(CH_3)_2$ group, this maximum in all cases is shifted toward the red (by 18-20 mμ) in comparison with the maximum for compounds containing OH or OCH_3 groups; for the latter, differences in the position of this maximum are unimportant. To a lesser extent, the position of the short-wave maximum depends upon to which series the given compound belongs. This is particularly true of the first three series of compounds: the variation in the position of the maximum in analogous compounds of the various series in this case is only 2-4 mμ. As a rule, for the derivatives of p-nitrophenylacetic acid, this maximum is always found the farthest toward the red. For nitrobenzoyl derivatives, the short-wave maximum is shifted hyposochromically in comparison with the maxima for analogous compounds of the first three series, on the average by 6 mμ.

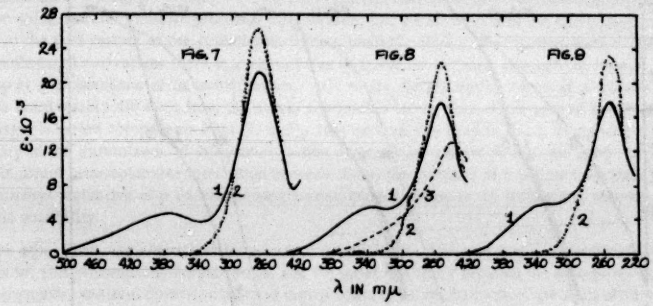


Fig. 7. 1) p-$O_2NC_6H_4CONHC_6H_4N(CH_3)_2$-p; 2) represents the sum of the absorption of p-$O_2NC_6H_4CONH_2$ and p-$CH_3CONHC_6H_4N(CH_3)_2$.

Fig. 8. 1) p-$O_2NC_6H_4CONHC_6H_4OH$-p; 2) represents the sum of the absorption of p-$O_2NC_6H_4CONH_2$ and p-$CH_3CONHC_6H_4OH$.

Fig. 9. 1) p-$O_2NC_6H_4CONHC_6H_4OCH_3$-p; 2) represents the sum of the absorption of p-$O_2NC_6H_4CONH_2$ and p-$CH_3CONHC_6H_4OCH_3$.

We find the same short-wave maxima on the absorption curves constructed on the basis of the sums of absorption of two suitably selected components, of which one contains an electron acceptor (p-$O_2NC_6H_4CH_3$) and the other an electron donor (p-$CH_3CONHC_6H_4$ A) system, such as, for example, for the compounds we have examined (Figs. 4, 5, 6).* Thus, the origin of the short-wave maximum for these compounds is associated with the presence of two separate chromophore systems in them — an electron donor system and an electron acceptor system, which can be especially clearly seen on Fig. 4.

However, this applies only to compounds of the first three series. As for the nitrobenzoyl derivatives, their absorption curves are considerably different from the summary curves of correspondingly selected components (p-$O_2NC_6H_4CONH_2$ + p-$CH_3CONHC_6H_4$ A) and they differ first of all by the presence of a second long-wave maximum (Figs. 7, 8, 9).

For compounds containing a supplementary electron donor group in the meta-position in relation to the NH group (Figs. 10-12), the short-wave maxima are split, that is, there are actually two maxima instead of one, the positions of these maxima being practically the same for analogous derivatives of the first three series of compounds. These two maxima correspond to the two maxima which may be observed on the absorption curves obtained on the basis of the sum of the absorption of two separate components (Figs. 13 and 14), and, therefore, in this case too, they are the results of the superposition of two separate bands, corresponding to two chromophore systems; our attention is drawn to the fact that for compounds containing a m-$N(CH_3)_2$ group, the maximum on the right, that is, the maximum corresponding to the electron donor component, is expressed considerably more intensely than in the summary curve. In the case of the hydroxy derivative, this difference in the intensity of the maxima is considerably less.

* Instead of p-nitrotoluene, it is possible to use the amide of p-nitrohydrocinnamic acid. The summary curve, obtained in this case, for the absorption, is essentially not different from the summary curve given by us.

For nitrobenzoyl derivatives, the maximum, corresponding to the electron acceptor component (the left), is expressed very weakly and is essentially a stage whose position may be determined only approximately and which is shifted hypsochromically in comparison with the corresponding maxima of the first three series of compounds (Figs. 10-12). The absorption curves of the nitrobenzoyl derivatives in this case, too, are considerably different, especially in the long-wave part, from the absorption curves constructed on the basis of the sum of the absorption of corresponding components (Figs. 15 and 16).

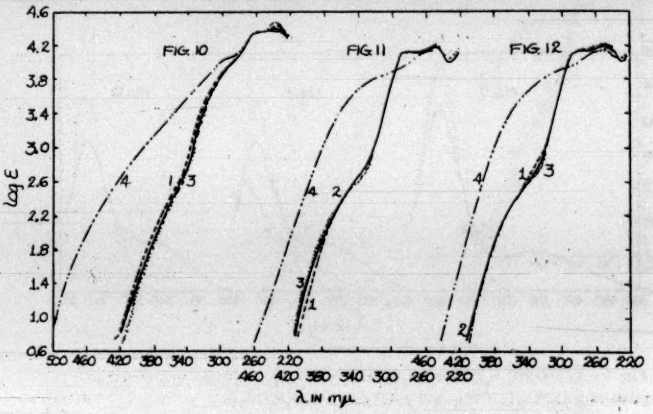


Fig. 10. 1) Npha – $N(CH_3)_2$-m; 2) Nhc – $N(CH_3)_2$-m; 3) Nphb – $N(CH_3)_2$-m; 4) Nbz – $N(CH_3)_2$-m.

Fig. 11. 1) Npha – OH-m; 2) Nhc – OH-m; 3) Nphb – OH-m; 4) Nbz – OH-m.

Fig. 12. 1) Npha – OCH_3-m; 2) Nhc – OCH_3-m; 3) Nphb – OCH_3-m; 4) Nbz – OCH_3-m.

(Npha = p-$O_2NC_6H_4CH_2CONHC_6H_4$; Nhc = p-$O_2NC_6H_4CH_2CH_2CONHC_6H_4$; Nphb = p-$O_2NC_6H_4CH_2CH_2CH_2CONHC_6H_4$; Nbz = p-$O_2NC_6H_4CONHC_6H_4$).

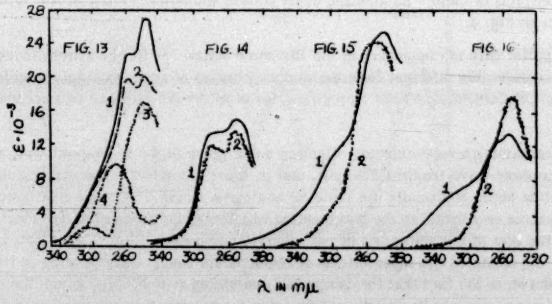


Fig. 13. 1) p-$O_2NC_6H_4CH_2CH_2CONHC_6H_4N(CH_3)_2$-m; 2) represents the sum of the absorption of 3 and 4; 3) m-$CH_3CONHC_6H_4N(CH_3)_2$; 4) p-$O_2NC_6H_4CH_3$.

Fig. 14. 1) p-$O_2NC_6H_4CH_2CH_2CONHC_6H_4OH$-m; 2) represents the sum of the absorption p-$O_2NC_6H_4CH_3$ and m-$CH_3CONHC_6H_4OH$.

Fig. 15. 1) p-$O_2NC_6H_4CONHC_6H_4N(CH_3)_2$-m; 2) represents the sum of the absorption p-$O_2NC_6H_4CONH_2$ and m-$CH_3CONHC_6H_4N(CH_3)_2$.

Fig. 16. 1) p-$O_2NC_6H_4CONHC_6H_4OH$-m; 2) represents the sum of the absorption p-$O_2NC_6H_4CONH_2$ and m-$CH_3CONHC_6H_4OH$.

The presence in the absorption curves for the nitrobenzoyl derivatives of a second – long-wave – maximum which is sharply different from the absorption curves of the analogous compounds of the other three series, is, evidently, to be explained by the possibility of the transmission of influence between the separate chromophore systems through the CONH group, or as a result of its isomerization to $-C(OH)=N-$, or as a consequence of electromeric transformation [4]:

The absence of a long wave maximum for the N-methyl derivative of p-(4-nitrobenzoyl)-aminophenol (Fig. 11), in which the electromeric process is also possible, but the isomerism of the $CON(CH_3)$ group is impossible, indicates that the first variant of the explanation is more probably correct, that is, that there is a possibility that in the p-nitrobenzoyl derivatives there is a transmission of influence between chromophore systems through the CONH group as a consequence of its isomerization. As a result, the absorption curves of p-nitrobenzoyl derivatives proved to be considerably different from the curves constructed on the basis of the sum of the absorption of separate, correspondingly selected components (Figs. 7, 8, 9). It is necessary to keep in mind, along with this, however, that the possibility of the transmission of influence between chromophore systems through the bonds does not exclude the possibility of direct intermolecular interaction between them; the presence of a yellow coloration in the above-indicated N-methyl derivative of p-(4-nitrobenzoyl)-aminophenol, taken in the solid state, may be considered evidence of this possibility.

On the other hand, the absence of long-wave maxima for the derivatives of p-nitrophenylacetic, p-nitrohydrocinnamic, and p-nitrophenylbutynic acids, and the great similarity between the absorption curves of all three series of compounds, and also their similarity to curves constructed on the basis of the sums of the absorption of separate components, may be considered as evidence that interaction does not take place between the chromophore systems through the connecting benzene ring group, even in the case of derivatives of p-nitrophenylacetic acid, where the possibility of isomerization might be assumed. Thus, the main cause of the coloration of the compounds which have been examined should be sought in the direct interaction between the electron acceptor and electron donor systems, with the help of the forces of the external field. This interaction is fully manifested only in substances in the solid state; in solutions, on the other hand, it is disrupted to a considerable extent, and therefore, the absorption curves in this case do not make it possible to judge the relative depth of the coloration of the compounds which are being examined. This can also explain the fact that the regularity in the change of the coloration, which is observed on the transition from one series of compounds to another, is manifested only when the compounds are in the solid state, but not when they are in solution. The small rise of the lower (long-wave) side of the curve, which is especially noticeably manifested for the $N(CH_3)_2$ derivatives of p-nitrophenylacetic acid (Fig. 1, curve 1), and the OH derivative of p-nitrohydrocinnamic acid (Fig. 2, curve 2), may be considered as evidence of the fact that in a dilute solution (10^{-3} M) intermolecular interaction may, nevertheless, be manifested to some small degree. Here, it is interesting to note the following fact: the derivative p-nitrohydrocinnamic acid, containing the p-$N(CH_3)_2$ group, is colored more deeply in the solid state than the corresponding derivative of p-nitrophenylacetic acid (the first, in the form of a powder, is yellowish-orange in color, the second is yellow-orange); this is also confirmed by reflection spectra (see our preceding article [1]); however, in solution, the reverse phenomenon is observed – solutions of the derivative of p-nitrohydrocinnamic acid in pyridine, benzyl alcohol, and acetone are colored less deeply than the corresponding solutions of the derivative of p-nitrophenylacetic acid; this may be detected even directly with the eyes, and it is also indicated by the absorption curves: the absorption curve of the first of the indicated compounds (in particular in its long-wave part) is shifted hypsochromically in relation to the absorption curve of the second compound (Fig. 1). On the other hand, the absorption curves of the same derivative of p-nitrohydrocinnamic acid and the derivative of p-nitrophenylbutyric acid which corresponds to it, are very similar to each other, and are almost completely superimposed on each other, although the visible coloration of the first of them in the solid state is considerably deeper than the coloration of the second (yellowish-orange in the first, orange-yellow in the second). Hence, it is possible to reach the conclusion that the intermolecular interaction which is observed in solution, in analogous compounds of various series, is not accomplished to the same extent, even in solutions of the same molar concentration.

The results of the intermolecular interaction which takes place in the solution would seem to indicate the independence of these solutions of Beer's law. For the majority of the compounds, (mainly those containing an $N(CH_3)_2$ or an OH group), as a rule, a small lack of correspondence in the values of absorption is observed, even on the transition from concentrations of 10^{-3}-10^{-4} M. However, the possibility is not excluded that this is the

result of changes in the size of the slit in the measuring apparatus, which take place on the transition from one concentration of the solution to another. Significant deviations from Beer's law were detected in more concentrated pyridine solutions ($2 \cdot 10^{-2}$ and $3 \cdot 10^{-3}$ M) for the derivatives of p-nitrophenylacetic acid and p-nitrohydrocinnamic acid, containing an $N(CH_3)_2$ group in the para-position (Fig. 17). In this case, it developed that for both compounds, solutions of smaller concentration ($3 \cdot 10^{-3}$ M) gave larger extinction coefficients (ϵ) than solutions of larger concentration ($2 \cdot 10^{-2}$ M). The explanation of this phenomenon, which appears strange at first glance, it seems to us should be sought in the fact that on the increasing of the concentration of the solution, the process of complex formation may lead not only to an increase in the number of interacting molecules, but also to the further combination of the colored particles which have already been formed as a result of this interaction. It is all the more probable that each of the molecules contains, at the same time, both electron acceptor and electron donor systems. As a result, it may also prove that in more concentrated solutions, the relative quantity of colored particles may be less than in more dilute solutions.

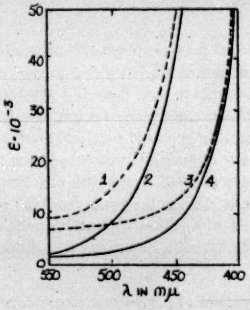


Fig. 17.
1) $p\text{-}O_2NC_6H_4CH_2CONHC_6H_4N(CH_3)_2$-p in pyridine $3 \cdot 10^{-3}$ m;
2) $p\text{-}O_2NC_6H_4CH_2CONHC_6H_4N(CH_3)_2$-p in pyridine $2 \cdot 10^{-2}$ m;
3) $p\text{-}O_2NC_6H_4CH_2CH_2CONHC_6H_4N(CH_3)_2$-p in pyridine $3 \cdot 10^{-3}$ m;
4) $p\text{-}O_2NC_6H_4CH_2CH_2CONHC_6H_4N(CH_3)_2$-p in pyridine $2 \cdot 10^{-2}$ m.

Spectroscopic measurement. The absorption spectra were measured by us on a Beckmann spectrophotometer. As a solvent, we used alcohol which had been preliminarily distilled in a fractionation column. The following concentrations of solutions were used in the spectroscopic measurements: 10^{-3} and 10^{-4} M for compounds of all four series containing the $N(CH_3)_2$ group, and for p-nitrotoluene; $2 \cdot 10^{-3}$ and 10^{-4} M for all compounds containing an OCH_3 or OH group; 10^{-2}, 10^{-3} and 10^{-4} M for components containing the electron donor system $CH_3CONHC_6H_4$ A and p-nitrobenzamide. The visible part of the spectrum in more concentrated pyridine solutions was measured on a universal monochromatic analyzer* (for verification of Beer's law).

SUMMARY

1. The absorption curves of the arylamides of p-nitrophenylacetic, p-nitrohydrocinnamic and γ-(p-nitrophenyl)-butyric acids are quite close to each other and differ quite radically from the corresponding absorption curves of the arylamides of p-nitrobenzoic acid.

2. With the presence of an electron donor group (A) in the para-position in relation to the NH group, all of the absorption curves of the indicated first three series of compounds are characterized by the presence of one short-wave maximum, the position of which depends more on the character of the electron donor group than on which of the three series includes a given compound.

3. For compounds containing an additional electron donor group (A) in the meta-position to the NH group, the short-wave maximum is divided, that is, there are actually two maxima in this case.

4. The nitrobenzoyl derivative, besides the short wave maximum, has a second, longer-waved maximum, which is clearly expressed in compounds containing an electron donor group in the para-position, and which has the appearance of a larger, also clearly expressed stage, in compounds with the electron donor group in the meta-position.

5. The absorption curves, constructed on the basis of the sum of the absorption of two separate components, which are analogous in their composition to electron acceptor and electron donor chromophore systems, and which are contained in the first three series of the examined compounds, are very similar to the absorption curves of these compounds, which indicates the absence in the latter of intramolecular interaction between the individual chromophore systems.

* UM-2 model.

6. Thus, the presence of a short-wave maximum in the first three series of compounds is the result of the superposition of two maxima, corresponding to two separate chromophore systems – the electron donor and electron acceptor systems.

7. The absorption curves of the p-nitrobenzoyl derivatives are distinguished quite strongly from the absorption curves constructed on the basis of the sum of the absorption of correspondingly selected components, mainly by the presence of a long wave maximum. The latter may be considered as evidence of the fact that in the nitrobenzoyl derivatives, the interaction between the electron donor and the electron acceptor systems may be accomplished not only by intermolecular action, but also as a result of intramolecular action, which is due to the isomerization of the $-CONH$ group to the $-C(OH)=N-$ group.

8. The small rise of the lower (long-wave) part of the curve, which is observed in certain of the compounds of the first three series should be considered a result of the intermolecular interaction which may take place to a small extent in dilute solutions, too.

9. The considerable deviations from Beer's law, which may be observed for some of the investigated compounds, using them in more concentrated solutions, may be considered as evidence of the presence of intermolecular interaction in the solution.

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* See Consultants Bureau Translation, page 769.

THE SYNTHESIS OF

3-(β-HYDROXYETHYL)-4-(β-CARBETHOXYETHYL)-N-ACETYLPIPERIDINE

M. V. Rubtsov

The method of preparation of homomeroquinene [1], described in 1945, is very complicated and is far from the possibility of practical use; therefore, the seeking of new means for the synthesis of this compound is very desirable. Our investigation in this direction led to the working out of a method for the preparation of 3-(β-hydroxyethyl)-4-(β-carbethoxyethyl)-N-acetylpiperidine, which may prove to be convenient for the synthesis of homomeroquinene.

We used 3-(β-chloroethyl)-4-methyl-2,6-dichloropyridine (trichloroeollidine) as a starting material; its synthesis has been described in the literature [2]; in the literature article, the yield of this product was 25.9% calculated on the α-acetobutyrolactone. Certain changes introduced by us in the individual stages of the synthesis enabled us to raise the total yield of trichlorocollidine to 39.1%.

In carrying out of the first stage of the reaction, we used cyanogen acetamide instead of cyanogen acetic ester, which led to the raising of the yield from 52 to 73%.

The second stage – the formation of the derivative of dihydrofuran – presents considerable difficulties on increasing of the scale of the work, which are associated with the utilization of hydrochloric acid under pressure.

The simplification in this stage was achieved by the use of 65% sulfuric acid, which allowed to us carry out the reaction in an open system with a reflux condenser.

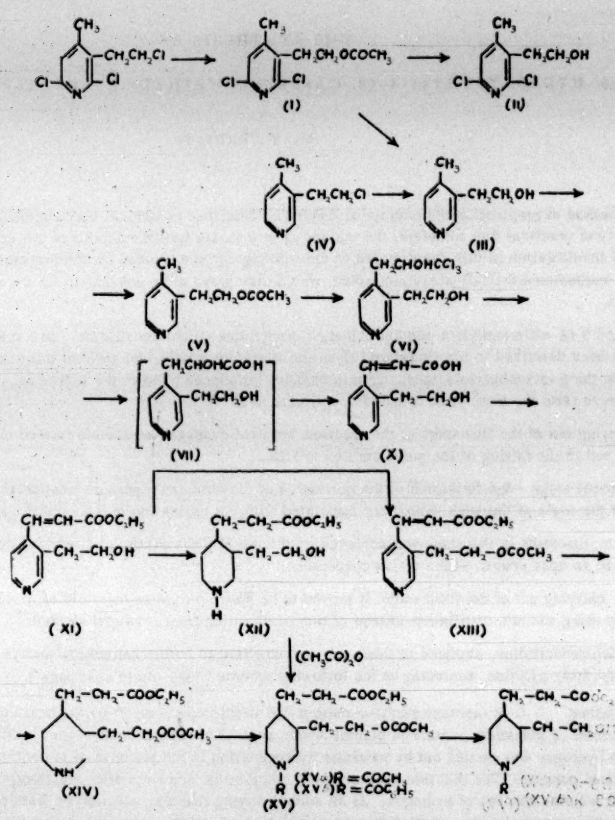
On carrying out of the third stage, it proved to be possible to raise the yield of trichlorocollidine from 57 to 67%, by using vacuum distillation instead of recrystallization from isopropyl alcohol.

The trichlorocollidine, obtained in this way, was subjected to further conversion to 3-(β-hydroxyethyl)-4-(β-carbethoxyethyl)-pyridine, according to the following scheme. [See top of next page.]

We obtained 3-(β-acetoxy ethyl)-4-methyl-2,6-dichloropyridine (I) by the heating of trichlorocollidine with an excess of potassium acetate in glacial acetic acid. The replacement of the chlorine in the obtained compound by hydrogen was carried out by catalytic hydrogenation in the presence of palladium black in methanol, under normal pressure. The reaction does not go to completion, and stops after the absorption of approximately 60% of the required amount of hydrogen. As an accompanying reaction, alcoholysis takes place; under the conditions of the experiment, the reaction goes to completion. From the reaction mixture the following compounds were isolated: 3-(β-hydroxyethyl)-4-methylpyridine (III) and 3-(β-hydroxyethyl)-4-methyl-2,6-dichloropyridine (II). The latter, on hydrolysis under the same conditions, forms (III), but the reaction, as in the first case, does not go to completion. The hydrogenation, evidently, is slowed down by the reaction product which is formed, since the catalyst does not lose its activity on being used, and may be used many times for the reduction of successive new portions of the dichloro-derivative.

The formation of (III) was accomplished also by the hydrolysis of 3-(β-chloroethyl)-4-methylpyridine (IV), which was obtained from trichlorocollidine by Stevens' method [2], by catalytic hydrogenation in the presence of palladium black. For the hydrolysis, hydrochloride (IV) is required, the process being carried out in a sealed tube at 140-150°. Attempts to carry out the hydrolysis of (IV) in a weakly alkaline medium at 100° led to the formation of a tarry dark-brown mass, which was, evidently, a mixture of quaternary salts.

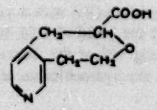
On the condensation of 3-(β-hydroxyethyl)-4-methylpyridine (III) with chloral, we obtained 3-(β-hydroxyethyl)-4-(γ,γ,γ-trichloro-β-hydroxypropyl)-pyridine (VI) with a yield of 20%. The use of 3-(β-acetoxyethyl)-4-methylpyridine (V) for the condensation doubles the yield of 3-(β-hydroxyethyl)-4-(γ,γ,γ-trichloro-β-hydroxypropyl)-pyridine (VI). A better yield, constituting 71% of the theoretical, calculated on the substance going into the reaction, was obtained on the utilization of the hydrochloride of (V).



For the preparation of 3-(β-hydroxyethyl)-4-(β-carboxyvinyl)-pyridine (X) from 3-(β-hydroxyethyl)-4-(γ,γ,γ-trichloro-β-hydroxypropyl)-pyridine (VI), the latter was subjected to the action of an alcoholic solution of potassium hydroxide with boiling; then the excess alkali was acidified with acetic acid. It has been assumed that the reaction will take place according to the scheme: (VI) → (VII) → (X).

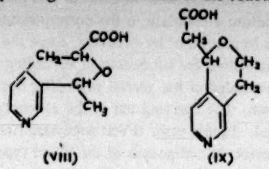
However, instead of the expected (X), from the reaction product were isolated two isomeric acids (A and B) which corresponded to formula (X) in their composition, but which did not contain either a double bond or an alcohol group.

The splitting off of water from 3-(β-hydroxyethyl)-4-(β-carboxy-β-hydroxyethyl)-pyridine (VII) may take place at the expense of the two hydroxyl groups, with the formation of an internal oxide, for example:



However, such a reaction mechanism seems to us to be improbable, since it leads to the formation of a seven-membered ring; at the same time, it is known that glycols, containing more than five carbon atoms between the hydroxyl groups, form only six-membered rings on the splitting off of water [3, 4].

In our case, on the splitting off of water from (VII), we should also expect the formation of a six-membered ring, either 3,4-(3',4'-pyridino)-6-methyldihydropyran-2-carboxylic acid (VIII), or 3,4-(3',4'-pyridino)-dihydropyran-2-acetic acid (IX), being formed, depending on the direction of the reaction:



(VIII) (IX)

The acids obtained by us, evidently, are either structural isomers [(VIII) and (IX)] or the cis- and trans-forms of (VIII). Their properties are given in Table 1.

TABLE 1

Designation	Temperature		Characteristic features
	of melting	of boiling at 0.3 mm	
Acid A	274-275°	–	Very difficultly soluble in water; is esterified with difficulty.
Acid B	188-192	–	Soluble in water; is easily esterified.
Ester of acid A		130-131°	The hydrochloride (m.p. 175-177°)
Ester of acid B		126-128	The hydrochloride (m.p. 141-143°) was vacuum distilled without decomposition.

The formation of acids A and B from 3-(β-hydroxyethyl)-4-(γ,γ,γ-trichloro-β-hydroxypropyl)-pyridine (VI) was accomplished in two stages. The first stage, as a result of which is formed 3-(β-hydroxyethyl)-4-(β-carboxy-β-hydroxyethyl)-pyridine (VII), undoubtedly takes place in an alcohol-alkali medium. The second stage – the splitting off of water, evidently takes place in an aqueous medium on the acidification of the alkaline solution.

If the second stage were to take place also in an alcohol-alkalin medium, the obtaining of 3-(β-hydroxyethyl)-4-(β-carboxyvinyl)-pyridine (X) would be impossible according to this method. However, we succeeded in preparing this compound, using more rigid conditions of alkaline dehydration. For this purpose, 3-(β-hydroxyethyl)-4-(γ,γ,γ-trichloro-β-hydroxypropyl)-pyridine (VI) was boiled with large excess of alcoholic alkali, then the alcohol was distilled off in a vacuum, and the residue, which contained the excess alkali, was heated over a boiling water bath at 15-20 mm. On the acidification of the reaction product with acetic acid, 3-(β-hydroxyethyl)-4-(β-carboxyvinyl)-pyridine (X) was isolated with a yield of 74%.

The obtained acid (X) was subjected to esterification, and the ethyl ester (XI) which was obtained thereby, was hydrogenated in the form of the hydrochloride in a solution of anhydrous alcohol in the presence of platinum black. The hydrogenation takes place slowly and leads to the formation of 3-(β-hydroxyethyl)-4-(β-carbethoxyethyl)-piperidine (XII).

For hydrogenation, it proved to be convenient to use 3-(β-acetoxyethyl)-4-β-carbethoxyvinyl)-pyridine (XIII), which is formed on the brief heating of 3-(β-hydroxyethyl)-4-(β-carbethoxyvinyl)-pyridine (X) with acetic anhydride, and which is easily purified by vacuum distillation. The acetyl derivative (XIII) is hydrogenated considerably more quickly than the original alcohol, and is converted to 3-(β-acetoxyethyl)-4-(β-carbethoxyethyl)-piperidine (XIV). This compound, like 3-(β-hydroxyethyl)-4-(β-carbethoxyethyl)-piperidine (XII), distills poorly in a vacuum, leaving a considerable amount (about 30%) of a brown mass, which is probably of a lactam character.

On the action of acetic anhydride on 3-(β-hydroxyethyl)-4-(β-carbethoxyethyl)-piperidine (XII) or on 3-(β-acetoxyethyl)-4-(β-carbethoxyethyl)-piperidine (XIV), 3-(β-acetoxyethyl)-4-(β-carbethoxyethyl)-N-acetylpiperidine (XVa) is formed.

For the conversion of (XVa) to 3-(β-hydroxyethyl)-4-(β-carbethoxyethyl)-N acetylpiperidine (XVIa), it was necessary to carryout the hydrolysis of the O-acetyl group under such conditions that the N-acetyl and the carbethoxyl groups remained untouched. The most suitable method for this purpose is alcoholysis, which, as is known, is easily accomplished by the use of sodium alcoholate in the corresponding alcohol. However, in our case, the use of sodium ethylate could lead to the formation of by-products, since the presence of the N-acetyl group, and two carboxyl groups created favorable conditions for condensation according to a reaction like the Claissen reaction. In addition, the possibility was not excluded of the partial saponification of the carbethoxyl and N-acetyl groups on the working of the reaction product. The carrying out of the alcoholysis with an alcoholic solution of hydrogen chloride proved to be more useful. In this case, it was necessary first to clarify the following questions: 1) how easily does the alcoholysis take place in compounds of the given type; 2) to what extent does the splitting off of the acetyl group, linked with the nitrogen atom, take place in this process.

In order to clarify the first question, we carried out a series of experiments, using as a model the acetate of β-[2,6-dichloro-4-methylpyridyl-(3)]-ethanol (I). This compound has a structure close to that of the investigated compound, and at the same time, does not form a hydrochloride.

The acetate was mixed with an alcoholic solution of hydrogen chloride, taken in such a quantity that for 1 mole of the acetate, 30 moles of alcohol and 0.05, 0.1 or 0.2 moles of hydrogen chloride were needed. The mixture was boiled for 1.5 hours, then the alcohol was distilled off over a water bath, and to the residue was added an additional amount of anhydrous alcohol, with subsequent distillation. The distillate contained hydrogen chloride and ethyl acetate. The hydrogen chloride was back-titrated with a 1 N solution of sodium hydroxide, after which the ethyl acetate was saponified by the action of an excess of 1 N sodium hydroxide, with boiling for 15 minutes. According to the amount of sodium hydroxide which was needed for the saponification of the ethyl acetate, we established the amount of the original product which underwent alcoholysis. The results of the experiments are given in Table 2 (Experiments 1, 2, 3, 4).

As is evident from the data of Table 2, the alcoholysis takes place with a yield of about 90% on the utilization of 0.1 mole of hydrogen chloride per 1 mole of the ester.

For the clarification of the influence of the given conditions on the splitting off of the acetyl group linked with the nitrogen atom, we carried out analogous experiments with N-acetylpiperidine; it became clear from these experiments that the N-acetyl group, under the conditions of the experiment, was affected to only an insignificant degree; the formation of ethyl acetate constituted about 2% on the utilization of 0.1 mole of hydrogen chloride, and was raised to 3% on the utilization of 0.2 mole of hydrogen chloride.

N-Benzoylpiperidine proved to be still more stable; it was saponified about 2% on the utilization of 0.4 mole of hydrogen chloride, which was established according to the amount of the hydrochloride of the piperidine which was formed.

On working with an alcoholic solution of hydrogen chloride of a mixture of acetylpiperidine and the acetate of β-[2,6-dichloro-4-methylpyridyl-(3)]-ethanol, the rate of the alcoholysis is reduced somewhat, evidently, due to the formation of the hydrochloride of N-acetylpiperidine.

These preliminary experiments made it possible to carry out the alcoholysis of 3-(β-acetoxyethyl)-4-(β-carbethoxyethyl)-N-acetylpiperidine (XVa) under conditions which allowed us to obtain 3-(β-hydroxyethyl)-4-(β-carbethoxyethyl)-N-acetylpiperidine (XVIa) with a yield of about 80%.

The separation of the alcohol (XVIa) which was formed, from admixtures of the original acetate (XVa) did not present difficulties, since the acetate is easily extracted from an aqueous solution with ether, while the alcohol remains in the aqueous sblution, from which it is then extracted with chloroform and is obtained completely pure by the distilling off of the latter.

Correspondingly, the N-benzoyl derivative (XVIb) was prepared by means of the benzoylation of 3-(β-acetoxyethyl)-4-(β-carbethoxyethyl)-piperidine (XIV) with the subsequent alcoholysis of the 3-(β-acetoxyethyl)-4-(β-carbethoxyethyl)-N-benzoyl piperidine (XVa) which is formed.

TABLE 2

The Splitting Off of an Acetyl Group from O- and N-Acetyl Piperidine (A – acetate of β-[2,6-dichloro-4-methyl-pyridyl-(3)]-ethanol; B – N-acetylpiperidine)

Expt. No.	Designation of substance	Relative quantity (in moles)			Length of heating (in hours)	Percentage of the splitting off of the acetyl group
		acetyl derivative	alcohol	HCl		
1	A	1	30	0.05	1.5	60.0
2	A	1	30	0.1	1.5	89.5
3	A	1	30	0.2	1.5	90.0
4	A	1	30	0.4	1.5	89.0
5	B	1	30	0.1	1.5	1.7
6	B	1	30	0.2	1.5	3.0
7	A	1	30	0.1	1.5	79.0
	B	1	30			
8	A	1	30	0.1	4.5	91.4
	B	1	30			
9	A	1	30	0.2	1.5	85.0
	B	1	30			
10	A	1	30	0.2	4.5	91.5
	B	1	30			
N-benzoylpiperidine		1	30	0.4	2	1.9
		1	30	0.8	1.5	4.0

EXPERIMENTAL

2,6-Dichloro-3-(β-acetoxyethyl)-4-methylpyridine (I). Into a three-necked, round-bottomed flask, equipped with a stirrer, a reflux condenser, and a thermometer, was charged 196 g of anhydrous potassium acetate, 180 ml of glacial acetic acid, and 224.5 g of 2,6-dichloro-3-(β-chloroethyl)-4-methylpyridine. The mixture was heated with weak boiling (the temperature of the mixture was 175°) and stirring for 10 hours.

The reaction mixture at first had two layers: the lower layer was a solution of potassium acetate in acetic acid, and the upper was the original substance. As the reaction went on, the upper layer gradually became smaller, and at the same time, a potassium chloride precipitate was formed. The temperature at which the reaction mixture boiled was lowered over a period of 10 hours to 150°. The hot mixture was filtered from the potassium chloride, and the precipitate was washed with glacial acetic acid. Then, the filtrate was concentrated until the temperature of the reaction mixture rose to 175°, after which the reaction mixture was boiled with a reflux condenser for 10 more hours; at this point, some more potassium chloride was again isolated. The acetic acid was distilled off in a vacuum over a water bath, and the residue was mixed with 500 ml of cold water. The oil which was isolated was extracted with ether, the extract was washed with a saturated solution of soda and dried with potash. After the driving off of the ether, the residue was distilled at a pressure of 11 mm. The following fractions were gathered: the first, 140-181°, 26 g; the second, 181-184°, 201 g.

The first fraction was a mixture of the original substance with the final reaction product. The second fraction was pure 2,6-dichloro-3-(β-acetoxyethyl)-4-methylpyridine. The yield was 81%. The product is a colorless oil, quite soluble in alcohol, ether, acetone and chloroform.

4.079 mg sub.: 7.219 mg CO_2; 1.670 mg H_2O. 0.1760 g sub.: 14.28 ml 0.1 N $AgNO_3$ (according to Stepanov). Found %: C 48.26; H 4.58; Cl 28.71. $C_{10}H_{11}O_2NCl_2$. Calculated %: C 48.40; H 4.47; Cl 28.61.

3-(β-Hydroxyethyl)-4-methylpyridine (III). To a solution of 192 g of 2,6-dichloro-3-(β-acetoxyethyl)-4-methylpyridine in 600 ml of methanol, was added a solution of 15 g of palladium chloride in 37 ml of concentrated hydrochloric acid and 50 ml of water, and the mixture was hydrogenated at room temperature under a pressure of 50-70 cm water column. At first the absorption of hydrogen took place rapidly, then it slowed down, and practically stopped after the absorption of about 60% of the required hydrogen. The solution was filtered from the catalyst, the methanol was distilled off, the hydrochloric acid was driven off in a vacuum over a boiling water

bath. To the remaining reaction mixture was added water, three times, 100 ml each time, with subsequent vacuum distillation for the driving off of the remnants of the free hydrochloric acid. The reaction product, which was a mixture of 3-(β-hydroxyethyl)-4-methylpyridine (III) and 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine (II), was mixed with 200 ml of water and the dichloro derivative was extracted with ether 6 times (150 ml each time). Then the aqueous solution was worked with an equal volume of 50% potassium hydroxide, and the oil which was separated was extracted with chloroform, and the extract was dried with potash. After driving off of the chloroform, the residue was vacuum distilled at 13 mm. 63.2 g of a colorless oil was obtained; its boiling point was 159-161°. On cooling, the oil crystallized; the melting point of the crystals was 65.5-67°. On analysis, this substance proved to be 3-(β-hydroxyethyl)-4-methylpyridine. The yield was 59.5%.

3.346 mg sub.: 8.575 mg CO_2; 2.460 mg H_2O. 8.371 mg sub.: 6.09 ml 0.01 N H_2SO_4 (Kjeldahl). Found %: C 69.89; H 8.22; N 10.13. $C_8H_{11}ON$. Calculated %: C 70.03; H 8.09; N 10.21.

The substance is very soluble in water, alcohol, chloroform, acetone and benzene, difficultly soluble in ether and petroleum ether. On the dilution of its benzene solution with ether, colorless, prismatic flakes are isolated; from an aqueous solution, the substance is isolated by alkali in the form of an oil.

The ether extract which was obtained above was dried with potash, the ether was distilled off, and the residue was vacuum distilled at 11 mm. 56.9 g of a colorless oil was gathered; it boiled at 182-184°. The oil quickly crystallized; the melting point of the crystals was 73.5-75°. According to analysis this substance is 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine (II). The yield was 35.7%.

2.969 mg sub.: 5.052 mg CO_2; 1.160 mg H_2O. 0.1916 g sub.: 13.48 ml 0.1 N $AgNO_3$ (according to Stepanov). Found %: C 46.41; H 4.37; Cl 34.2. $C_8H_9ONCl_2$. Calculated %: C 46.60; H 4.40; Cl 34.42.

The substance is quite soluble in chloroform, alcohol, ether, acetone and benzene; it is difficultly soluble in petroleum ether. From hot benzene it is crystallized, upon cooling, in the form of white needles.

Like 2,6-dichloro-3(β-acetoxyethyl)-4-methylpyridine (I), the substance, on catalytic reduction in the presence of palladium, is converted into 3-(β-hydroxyethyl)-4-methylpyridine.

The hydrolysis of 3-(β-chloroethyl)-4-methylpyridine. A solution of 2.88 g of the hydrochloride of 3-(β-chloroethyl)-4 methylpyridine* in 30 ml of water was heated in a sealed tube for 3 hours at 140-150°. Then, to the solution was added 2.52 g of sodium bicarbonate. The suspension which was isolated was extracted with ether. To the aqueous solution was added 40 ml of a 40% solution of sodium hydroxide, the oil which was separated was extracted with chloroform and the extract was dried with potash. After driving off of the chloroform, 1.64 g of a light-yellow oil was obtained; the oil crystallized on cooling; the melting point of the crystal was 63-65°. A sample, crystallized from benzene (90-100°), melted at 65.5-67° and did not give a depression of the melting point with 3-(β-hydroxyethyl)-4-methylpyridine. The yield was 80%.

3-(β-Acetoxyethyl)-4-methylpyridine (V). A mixture of 46 g of 3-(β-hydroxyethyl)-4-methylpyridine and 51 g of acetic anhydride was heated for 40 minutes, with boiling. The cooled reaction mixture was dissolved in 600 ml of ether and was gently shaken in a separatory funnel with 300 ml of a 15% solution of soda in order to drive off the acetic acid. The aqueous layer was separated, washed twice with ether (100 ml each time). The ether extracts were added to the main ether solution and dried with potash. After distillation of the ether, the residue was vacuum distilled at 11 mm. A fraction boiling at 137-139° was gathered. The obtained substance was a colorless, clear oil, which is quite soluble in the ordinary organic solvents, and difficultly soluble in water. The yield was 56.7 g (94-3%).

6.560 mg sub.: 0.441 ml N_2 (19.5°, 731 mm). Found %: N 7.90. $C_{10}H_{13}O_2N$. Calculated %: N 7.82.

The hydrochloride consisted of colorless, joined prismatic flakes with a melting point of 101-103°. They are quite soluble in water, alcohol, and chloroform, and insoluble in ether.

6.548 mg sub.: 0.372 ml N_2 (24°, 739.3 mm). 6.900 mg sub.: 4.560 mg AgCl. Found %: N 6.37; Cl 16.35. $C_{10}H_{13}O_2N \cdot HCl$. Calculated %: N 6.49; Cl 16.47.

3-(β-Hydroxyethyl)-4-(γ,γ,γ-trichloro-β-hydroxypropyl)-pyridine (VI). A mixture of 55.5 g of 3-(β-acetoxyethyl)-4-methylpyridine, 63 g of chloral, 3.5 ml of piperidine and 2.2 ml of glacial acetic acid was heated for 17 hours at 82-86°. The reaction mixture was dissolved in 500 ml of 2 N hydrochloric acid, the solution was heated for 10 minutes with boiling, then it was cooled with cold water and quickly mixed with 700 ml of a

* Prepared from trichlorocollidine by Stevens' method [2].

15% soda solution. A brown oily substance was isolated, which quickly began to crystallize. The obtained crystalline substance was quite soluble in alcohol and in dilute hydrochloric acid, and very difficultly soluble in acetone, chloroform and ether. On the other hand, the oily substance which was separated at first, which is, evidently, a polymorphic modification of the crystalline substance, is much more soluble in ether; it is isolated from the solution in a stable crystalline form after a short time, in this case. Since the accompanying tarry admixtures are insoluble in ether, it proved to be possible to separate the product of condensation in the pure state. For this purpose, the oil which was separated on the alkalization of the solution, was immediately extracted with ether, and the ether solution was quickly transferred to a beaker. After 1-3 minutes, the separation of pale-yellow crystals began. After being allowed to stand for several hours, the residue was filtered and washed with ether. The melting point of the crystals was 164-166°. Yield 47.8 g (54.2%). After crystallization from alcohol, white, lustrous prisms, m.p. 166.5-168°. Readily soluble in methanol and ethanol, soluble in hot acetone, difficultly soluble in chloroform and ether.

According to analysis, the substance is 3-(β-hydroxyethyl)-4-(γ,γ,γ-trichloro-β-hydroxypropyl)-pyridine. The yield was 54.2%.

4.370 mg sub.: 6.809 mg CO_2; 1.699 mg H_2O. 3.450 mg sub.: 5.270 mg AgCl. Found %: C 42.49; H 4.35; Cl 37.79. $C_{10}H_{12}O_2NCl_3$. Calculated %: C 42.18; H 4.29; Cl 37.39.

The saponification of 3-(β-hydroxyethyl)-4-(γ,γ,γ-trichloro-β-hydroxypropyl)-pyridine. To a solution of 8 g of potassium hydroxide in 40 ml of anhydrous alcohol was added a solution of 5.68 g of 3-(β-hydroxyethyl)-4-(γ,γ,γ-trichloro-β-hydroxypropyl)-pyridine in 40 ml of anhydrous alcohol. The mixture was heated for 2 hours over a water bath at 70°. A copious potassium chloride precipitate was isolated. The temperature of the bath was lowered to 60°, and into the reaction mixture was passed carbonic acid until the gelatinous mass which had been formed at first was converted into a fine, crystalline powder. The residue, which was a mixture of potassium chloride and potassium bicarbonate, was filtered, washed with anhydrous alcohol, and the filtrate evaporated in a vacuum until dry. The residue was dissolved in 14 ml of water, the solution was acidified with 1.2 ml of acetic acid, and was allowed to stand for two hours at room temperature. The residue which was separated was filtered, washed with 3 ml of water, 3 ml of alcohol, then with 10 ml of ether, and dried in the air. 2 g of a white crystalline powder with a yellowish tint was obtained; it melted at 250-254° with decomposition (A). From the mother liquor, on standing for 24 hours, at 0° was isolated a light-yellow precipitate; 0.35 g of the precipitate was obtained; its melting point was 172-184°, decomposition taking place (B).

A substance with a melting point of 250-254° was recrystallized from hot water with carbon. Colorless joined prismatic flakes were obtained, which were quite soluble in dilute mineral acids and in dilute alkalis, difficultly soluble in water and in the ordinary organic solvents. Their melting point was 274-275° (with decomposition). This substance is a carboxylic acid, which has the composition $C_{10}H_{11}O_3N$. The properties of the obtained acid (the absence of a double bond and the alcohol hydroxyl) caused us to ascribe to it one of two isomeric formulas, which have an ether oxygen: 3,4-(3',4'-pyridino)-2-methyldihydropyran-6-carboxylic acid (VIII) or 3,4-(3',4'-pyridino)-dihydropyran-2-acetic acid (IX).

4.016 mg sub.: 9.128 mg CO_2; 2.015 mg H_2O. 7.917 mg sub.: 0.493 ml N_2 (20.5°, 741.5 mm). 0.1447 g sub.: 7.45 ml 1 N NaOH. Found %: C 61.99; H 5.61; N 7.06; equiv. 194.2. $C_{10}H_{11}O_3N$. Calculated %: C 62.18; H 5.70; N 7.18; equiv. 193.1.

The ethyl ester was prepared by the heating of the acid with a 6% alcohol solution of hydrogen chloride for 5 hours. A colorless oil was obtained, that boiled at 130-131° at 0.3 mm; it is quite soluble in the ordinary organic solvents. The presence of the hydroxyl group was not detected. On esterification about 30% of the acid taken was converted back.

d_4^{20} 1.1535, n_D^{20} 1.5230, MR_D 58.55. $C_{12}H_{15}O_3N$. Calculated 58.93.

4.504 mg sub.: 10.721 mg CO_2; 2.712 mg H_2O. 3.661 mg sub.: 0.214 ml N_2 (20°, 731 mm). Found %: C 64.92; H 6.74; N 6.54. $C_{12}H_{15}O_3N$. Calculated %: C 65.14; H 6.83; N 6.33.

The hydrochloride of the ethyl ester of acid A is a snow-white crystalline substance with a melting point of 175-177°, which is quite soluble in water, alcohol and chloroform.

4.100 mg sub.: 2.270 mg AgCl. Found %: Cl 13.69. $C_{12}H_{15}O_3N \cdot HCl$. Calculated %: Cl 13.77.

The investigation of substance B. The substance with a melting point of 172-184°, gathered from several experiments, was subjected to purification by means of repeated recrystallizations from water and from alcohol. The melting point, although it was raised, continued to be extended over a comparatively wide range (180-190°).

In order further to purify the substance, it was subjected to esterification by the action of an alcoholic solution of hydrogen chloride. The ester which was obtained by this process was a colorless oil, quite soluble in the ordinary organic solvents; its boiling point was 126-128° at 0.3 mm. The substance does not contain either a double bond, or a hydroxyl group, and is an isomer of the ethyl ester of acid A.

d_4^{20} 1.1465, n_D^{20} 1.5196, MR_D 58.60. $C_{12}H_{15}O_3N$. Calculated 58.93.

6.135 mg sub.: 14.726 mg CO_2; 3.820 mg H_2O. 5.004 mg sub.: 0.285 ml N_2 (20°, 731 mm). Found %: C 65.46; H 6.96; N 6.38. $C_{12}H_{15}O_3N$. Calculated %: C 65.14; H 6.83; N 6.33.

The hydrochloride is a white crystalline powder with a melting point of 141-143°. It is quite soluble in water, alcohol and chloroform. On heating in a vacuum it was distilled without decomposition.

6.235 mg sub.: 3.475 mg AgCl. Found %: Cl 13.79. $C_{12}H_{15}O_3N \cdot HCl$. Calculated %: Cl 13.77.

On saponification of the ethyl ester of acid B with a normal solution of sodium hydroxide, the free acid was obtained in the form of fine, white prisms, which melted at 188-192° with decomposition. The acid is quite soluble in dilute mineral acids and alkalis, is soluble in water (approximately 1:30), and is difficultly soluble in the ordinary organic solvents. According to analysis it has the same composition as acid A.

3.934 mg sub.: 8.926 mg CO_2; 2.002 mg H_2O. 4.157 mg sub.: 0.265 ml N_2 (19°, 740 mm). Found %: C 61.98; H 5.70; N 7.25. $C_{10}H_{11}O_3N$. Calculated %: C 62.18; H 5.70; N 7.18.

3-(β-Hydroxyethyl)-4-(β-carboxyvinyl)-pyridine (X). To a solution of 22 g of potassium hydroxide in 100 ml of anhydrous alcohol, was added a solution of 11.36 g of 3-(β-hydroxyethyl)-4-(γ,γ,γ-trichloro-β-hydroxypropyl)-pyridine in 80 ml of anhydrous alcohol. The mixture was heated for 3 hours over a water bath at 30-40° and then for one hour with boiling. A copious precipitate was isolated; it was potassium chloride. After cooling, the residue was filtered, washed with anhydrous alcohol, and the filtrate was evaporated in a vacuum at 120-155 mm over a water bath heated to 60°. When the alcohol had been distilled off, the residue was heated in a vacuum at 20 mm over a boiling water bath for two hours. The dry residue, which was a light-brown, glassy mass, was dissolved in 100 ml of 96% alcohol and into the obtained solution at 60-65° was passed a current of carbon dioxide, until the glassy mass which had been separated at first was converted into a fine crystalline powder ($KHCO_3$). The precipitate was filtered, the filtrate was evaporated in a vacuum, the precipitate was dissolved in 20 ml of water and acidified with 4.8 ml of 50% acetic acid. A white precipitate with a slight rosy tint was isolated. The mixture was allowed to stand for two hours at −10°, then the precipitate was filtered, washed with 4 ml of cold water, 8 ml of alcohol, and 15 ml of ether, and dried at 100°.

5.76 g (74.6%) of a white powder with a slight rosy tint was obtained; it melted at 200-201°. For analysis, the acid was recrystallized from water with carbon. It crystallized in the form of colorless nodules of fine needles; their melting point was 202-202.5°.

2.814 mg sub.: 6.408 mg CO_2; 1.476 mg H_2O. 4.392 mg sub.: 0.279 ml N_2 (21°, 746.5 mm). 6.557 mg sub.: 1.680 ml CH_4 (0°, 760 mm). Found %: C 62.10; H 5.86; N 7.25; OH 17.95. $C_{10}H_{11}O_3N$. Calculated %: C 62.18; H 5.70; N 7.18; OH 17.62.

The acid is very soluble in dilute mineral acids and in dilute alkalis, quite soluble in hot water (1:10), and is difficultly soluble in alcohol, and insoluble in ether. The test with permanganate indicated the presence of a double bond.

3-(β-Hydroxyethyl)-4-(β-carbethoxyvinyl)-pyridine (XI). A mixture of 21.23 g of 3-(β-hydroxyethyl)-4-(β-carboxyvinyl)-pyridine and 215 ml of a 4% alcohol solution of hydrogen chloride was heated with boiling until the full dissolution of the precipitate, after which the heating was continued for two more hours. On cooling, the hydrochloride of 3-(β-hydroxyethyl)-4-(β-carbethoxyvinyl)-pyridine was isolated. The precipitate was filtered, washed with a small amount of anhydrous alcohol, then with ether, and dried at 95°. It crystallized in the form of white nodules of needles with a slight rosy tint; their melting point was 174-175°. The yield was 24.32 g (85.8%).

0.2317 g sub.: 3.1 ml 0.1 N $AgNO_3$. Found %: Cl 13.92. $C_{12}H_{15}O_3N \cdot HCl$. Calculated %: Cl 13.77.

From the mother liquor, on evaporation in a vacuum, was isolated 2.9 g more of a less pure product with a melting point of 167-170°.

The base crystallized in the form of colorless prisms (from acetone) with a melting point of 100-101°; it is very soluble in chloroform, alcohol and boiling acetone (approximately 1:3), less soluble in cold acetone (approximately 1:20), and difficultly soluble in ether.

3.300 mg sub.: 7.904 mg CO_2; 2.060 mg H_2O. 6.434 mg sub.: 0.373 ml N_2 (20.5°, 733 mm). Found %: C 65.32; H 6.99; N 6.50. $C_{12}H_{15}O_3N$. Calculated %: C 65.14; H 6.83; N 6.33.

3-(β-Acetoxyethyl)-4-(β-carbethoxyvinyl)-pyridine (XIII). 4.2 g of 3-(β-hydroxyethyl)-4-(β-carbethoxyvinyl)-pyridine was mixed with 2.4 ml of acetic anhydride. The thick mixture, on spontaneous warming, quickly became a homogeneous solution. The solution was heated for forty-five minutes over a water bath, then it was cooled, diluted with 25 ml of ether, and washed with a 15% soda solution in order to drive off the acetic acid. After the drying of the ether solution with potash and the distilling off of the ether, the residue was vacuum distilled at 0.3 mm. 4.65 g of a colorless oil, boiling at 145-147° was gathered. The substance was quite soluble in alcohol, ether, acetone, chloroform and in dilute mineral acids. On long standing it crystallized (joined prisms); their melting point was 39-41°. The yield was 90%.

5.932 mg sub.: 0.285 ml N_2 (21°, 731.1 mm). Found %: N 5.37. $C_{14}H_{17}O_4N$. Calculated %: N 5.32.

The hydrochloride crystallized in the form of fine white needles (from acetone) with a melting point of 140.5-141.5°; it is formed on the action of an alcohol solution of hydrogen chloride and an ether solution of the base, or by the interaction of the hydrochloride of 3-(β-hydroxyethyl)-4-(β-carbethoxyvinyl)-pyridine with acetic anhydride, at 100° for two hours, with the subsequent dilution of the reaction mixture with dry ether. In the latter case, the yield constituted 96%.

0.2096 g sub.: 7.1 ml 0.1 N $AgNO_3$. Found %: Cl 12.01. $C_{14}H_{17}O_4N \cdot HCl$. Calculated %: Cl 11.83.

3-(β-Hydroxyethyl)-4-(β-carbethoxyethyl)-piperidine (XII). A mixture of 16.6 g of the hydrochloride of 3-(β-hydroxyethyl)-4-(β-carbethoxyvinyl)-pyridine, 120 ml of anhydrous alcohol and 1 g of platinum dioxide was hydrogenated under a pressure of 50-70 cm water column. As the hydrogenation took place, the hydrochloride was gradually dissolved. The hydrogenation was completed after 60 hours. The solution was filtered from the catalyst and evaporated in a vacuum. The residue, which was the hydrochloride of the product of hydrogenation, and which was a glassy mass, was dissolved in 120 ml of chloroform; to the solution was added 16 g of powdered potash and 5 ml of water, after which the mixture was shaken for two hours. Then, the chloroform solution was filtered, dried with potash, and the chloroform was distilled off in a vacuum. 14.8 g of a light yellow, thick oil was obtained; it is soluble in water, alcohol, ether, chloroform, and acetone. The yield was quantitative. 3 g of the substance was vacuum distilled at 0.3 mm. The following fractions were obtained: the first, 156-169°, 0.43 g; the second, 169-171°, 1.47 g. In the flask there remained a brown residue which was probably of a lactam character; its quantity was 1 g; the analysis of the second fraction is given below.

3.885 mg sub.: 8.930 mg CO_2; 3.544 mg H_2O. 5.732 mg sub.: 0.319 ml N_2 (21°, 733 mm). Found %: C 62.68; H 10.20, N 6.23. $C_{12}H_{23}O_3N$. Calculated %: C 62.83; H 10.11; N 6.11.

The substance is a thick, colorless oil; it does not form crystalline salts with picric, picrolonic, or hydrochloric acids with chloroplatinic acid, it gives an oil, which on standing for several days is converted into an orange, crystalline powder, which melts at 206-209° (with decomposition).

3-(β-Acetoxyethyl)-4-(β-carbethoxyethyl)-N-acetylpiperidine (XVa). 11.8 g of undistilled 3-(β-hydroxyethyl)-4-(β-carbethoxyethyl)-piperidine, described in the preceding experiment, was mixed with 20 ml of acetic anhydride, and the obtained solution was heated for two hours over a boiling water bath. Then, the acetic acid and the excess of acetic anhydride were distilled off at 15 mm, and the residue was distilled at 0.3 mm. Two fractions were gathered: the first, 165-181°, 3.2 g (19.8 %); the second, 181-184°, 11.5 g (71.2%). In the flask there remained an insignificant amount of a residue; the second fraction was a thick, colorless oil, quite soluble in the ordinary organic solvents and in dilute hydrochloric acid. On mixing with an equal amount of water, a homogeneous solution was formed, from which, on the further addition of water, an oil was again isolated. The extraction of the obtained mixture four times with ether led to the quantitative extraction of the substance. According to analysis the second fraction is 3-(β-acetoxyethyl)-4-(β-carbethoxyethyl)-N-acetylpiperidine. The yield was 71.2%.

d_4^{20} 1.1117, n_D^{20} 1.4833. MR_D 80.50. $C_{16}H_{27}O_5N$. Calculated 80.68.

6.227 mg sub.: 14.005 mg CO_2; 4.776 mg H_2O. 10.025 mg sub.: 0.400 ml N_2 (21.5°, 733.7 mm). Found %: C 61.34; H 8.58; N 4.54. $C_{16}H_{27}O_5N$. Calculated %: C 61 34, H 8.69; N 4.47.

3-(β-Acetoxyethyl)-4-(β-carbethoxyethyl)-piperidine (XIV). This compound was obtained by the hydrogenation of the hydrochloride of 3-(β-acetoxyethyl)-4-(β-carbethoxyvinyl)-pyridine (XIII) in anhydrous alcohol in the presence of platinum.

The hydrochloride of (XIV) is a light yellow, glassy mass, quite soluble in water, alcohol, acetone and chloroform.

The base is a colorless, mobile oil with a boiling point of 138-141° at 0.3 mm; it is quite soluble in alcohol, ether, acetone, chloroform, and water; from an aqueous solution it was isolated with a soda solution. It does not form crystalline salts with picric, picrolonic or hydrochloric acids.

d_4^{20} 1.0583, n_D^{20} 1.4718, MR_D 71.69. $C_{14}H_{25}O_4N$. Calculated 71.33.

3.563 mg sub.: 8.082 mg CO_2; 2.945 mg H_2O. 5.380 mg sub.: 0.256 ml N_2 (20.5°, 727 mm). Found %: C 61.80; H 9.23; N 5.30. $C_{14}H_{25}O_4N$. Calculated %: C 61.95; H 9.29; N 5.16.

On the working of the obtained compound with acetic anhydride, the corresponding N-acetyl derivative, described in the preceding experiment, was formed.

3-(β-Hydroxyethyl)-4-(β-carbethoxyethyl)-N-acetylpiperidine (XVIa). To a solution of 14.2 g of 3-(β-acetoxyethyl)-4-(β-carbethoxyethyl)-N-acetylpiperidine in 140 ml of 99.6% alcohol was added 1.14 ml of a 14.46% alcohol solution of hydrogen chloride, and the mixture was heated with weak boiling for five hours. Then the alcohol was distilled off over a water bath to one-fifth of the original volume, after which the distillation was carried out in a vacuum, at first at 150 mm, then at 30 mm. 130 ml of distillate was gathered; it contained ethyl acetate. A test showed that 9.65 ml of 1 N NaOH was required for the saponification of the ethyl acetate in 30 ml of the distillate; this constituted 92.2% of the theoretical. To the residue, after the driving off of the alcohol, was added 100 ml more of 99.6% alcohol, the solution was heated for one hour with boiling, after which the alcohol was again distilled off. 93 ml of the distillate was gathered. For the saponification of 31 ml of the distillate, 0.62 ml of 1 N NaOH was required.

The residue was heated in a vacuum at 15 mm and 80° for one hour. 12.42 g of a caramel-like, light yellow mass was obtained; it was mainly 3-(β-hydroxyethyl)-4-(β-carbethoxyethyl)-N-acetylpiperidine, with admixtures of the original product, the hydrochloride of 3-(β-hydroxyethyl)-4-(β-carbethoxyethyl)-piperidine and, possibly, the hydrochloride of 3-(β acetoxyethyl)-4-(β-carbethoxyethyl)-piperidine. In order to separate the hydrochlorides, the reaction mixture was mixed with 200 ml of dry ether and allowed to stand over night. Then, the clear solution was decanted, the residue was washed twice with dry ether and dried in a vacuum over a boiling water bath. The weight of the mixture of hydrochlorides was 1.49 g. From the ether solution, 10.9 g of a colorless, thick oil was obtained. For separation from the original product, the oil was mixed with 44 ml of water. The turbid solution which was formed was extracted four times with ether, 20 ml each time (extract I), then four times with chloroform, 15 ml each time (extract II).

The ether extract was washed with 20 ml of water, the aqueous extract was washed twice with ether, mixed with an equal volume of a saturated potash solution, and the suspension which was isolated was extracted with chloroform (extract III). All the extracts were dried with potash, the solvents were distilled off, and their residues driven off in a vacuum at 100°. From extract I was obtained 0.57 g of the original product, which constituted 4% of the quantity taken for the reaction. From extract II was obtained 9.72 g of a colorless, thick oil, which proved on analysis to be 3-(β-hydroxyethyl)-4-(β-carbethoxyethyl)-N-acetylpiperidine. The yield was 79%.

d_4^{20} 1.1170, n_D^{20} 1.4982, MR_D 71.19. $C_{14}H_{25}O_4N$. Calculated 71.43.

5.554 mg sub.: 12.661 mg CO_2; 4.563 mg H_2O. 8.654 mg sub.: 0.412 ml N_2 (21.5°, 723 mm). Found %: C 62.17; H 9.19; N 5.26. $C_{14}H_{25}O_4N$. Calculated %: C 61.95; H 9.29; N 5.16.

The substance is very soluble in water, alcohol, chloroform and acetone, less soluble in ether (approximately 1:12). Its boiling point is 199-202° (0.3 mm). It forms a caramel-like mass with phenyl isocyanate.

From extract III was obtained 0.3 g of a thick, almost colorless oil, which was, judging by its index of refraction (n_D^{20} 1.4950), less pure 3-(β-hydroxyethyl)-9-(β-carbethoxyethyl)-N-acetylpiperidine.

3-(β-Acetoxyethyl)-4-(β-carbethoxyethyl)-N-benzoylpiperidine (XVb). To a solution of 19 g of 3-(β-acetoxyethyl)-4-(β-carbethoxyethyl)-piperidine in 200 ml of chloroform, was added 15.5 g of powdered potash, and then 13.5 g of benzoyl chloride was added gradually with stirring (evolution of heat). When the temperature of the mixture fell to room temperature, 7.5 ml of water was added to it over a period of twenty minutes (evolution of heat), after which the reaction mixture was mixed for three hours at room temperature, and two hours with boiling. On cooling, the residue was filtered, the filtrate was separated from the water, dried with potash, the chloroform was distilled off, and the residue was vacuum distilled at 0.3 mm. 22.4 g of a light yellow, thick oil with a boiling point of 207-210° was obtained. The yield was 85.3%.

The substance is quite soluble in alcohol, ether, chloroform, and acetone, difficultly soluble in petroleum ether, insoluble in water.

d_4^{20} 1.1335, n_D^{20} 1.5190, MR_D 100.37. $C_{21}H_{29}O_5N$. Calculated. 100.17.

3.362 mg sub.: 8.361 mg CO_2; 2.303 mg H_2O. 7.041 mg sub.: 0.229 ml N_2 (20.5°, 743.5 mm). Found %: C 67.82; H 7.66; N 3.71. $C_{21}H_{29}O_5N$. Calculated %: C 67.70; H 7.79; N 3.73.

3-(β-Hydroxyethyl)-4-(β-carbethoxyethyl)-N-benzoylpiperidine (XVIb). To a solution of 23.5 g of 3-(β-acetoxyethyl)-4-(β-carbethoxyethyl)-N-benzoylpiperidine in 150 ml of anhydrous alcohol was added 19 ml of a 12% alcohol solution of hydrogen chloride, and the mixture was boiled for five hours with a reflux condenser. Then the alcohol was distilled off, and its residue driven off in a vacuum. The reaction mixture was again dissolved in 150 ml of anhydrous alcohol, the solution was heated with boiling for three more hours, after which the alcohol was driven off with the use of a vacuum in the final distillation. The residue, which was a thick, yellow oil, was extracted with ether three times, 150 ml each time, the ether extract was first washed three times with water, 20 ml each time, then with a saturated potash solution three times, 10 ml each time, and after this was dried with potash. From the ether extract was obtained 15.17 g of a thick, light yellow oil which had the odor of ethyl benzoate. For the driving off of the latter, the oil was dissolved in 15 ml of ethyl ether and was isolated by the addition of 45 ml of pentane. After decantation of the solvents, the remaining oil was washed with 35 ml of pentane, then subjected to repeated reprecipitation and finally dried in a vacuum at 80°. 13.62 g (65.3%) of a very thick, clear, light yellow oil was obtained. The substance was quite soluble in alcohol, ether, chloroform, and acetone, difficultly soluble in water (about 1.3%), insoluble in petroleum ether; its boiling point at 0.3 mm was 231-236° with slight decomposition.

d_4^{20} 1.1486, n_D^{20} 1.5378, MR_D 90.70. $C_{19}H_{27}O_4N$. Calculated 90.92.

3.569 mg sub.: 9.004 mg CO_2; 2.600 mg H_2O. 6.785 mg sub.: 0.264 ml N_2 (20.5°, 738 mm). Found %: C 68.75; H 8.15; N 4.35. $C_{19}H_{27}O_4N$. Calculated %: C 68.42; H 8.17; N 4.20.

SUMMARY

1. 3-(β-Hydroxyethyl)-4-(β-carbethoxyethyl)-N-acetylpiperidine, and the corresponding N-benzoyl derivative have been synthesized.

2. In the process of the synthesis, it has been established that on the saponification of 3-(β-hydroxyethyl)-4-(γ,γ,γ-trichloro-β-hydroxypropyl)-pyridine there is formed, depending upon the reaction conditions, either 3-(β-hydroxyethyl)-4-(β-carboxyvinyl)-pyridine, or bicyclic compounds, belonging, evidently, to the series of 3,4-(3',4'-pyridino-dihydropyran.

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THE ALKALOIDS OF GALANTHUS WORONOWI

III. THE STRUCTURE OF GALANTAMINE

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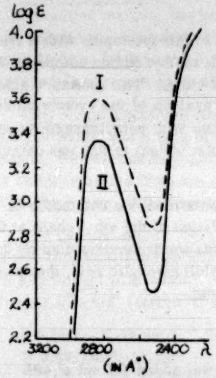
We reported earlier [1] on the isolation from Caucasian snowdrops (Galanthus) of a new alkaloid galantamine. As has been pointed out, this base, which has the composition $C_{17}H_{21}O_3N$ and which has a melting point of 126-127°, is an optically active ($[\alpha]_D$ −118.8°) tertiary base of an unsaturated character, which contains in its molecule one methoxyl, one methylimide, and one hydroxyl group of a nonphenolic character; the third oxygen atom of galantamine is found in a reaction-inactive form. The fact that galantamine was found together with the alkaloids galantine and lycorine [2] in the bulb of the Caucasian snowdrop suggested to us that there was a structural closeness between galantamine and these bases; this is confirmed by a comparative study of the absorption spectra of galantine and galantamine, which shows the almost complete coincidence of the absorption spectra of these alkaloids. Since galantine [3] and lycorine [4] belong to the alkaloids of the phenanthridine series, one might expect the presence of this same main nucleus in galantamine too.

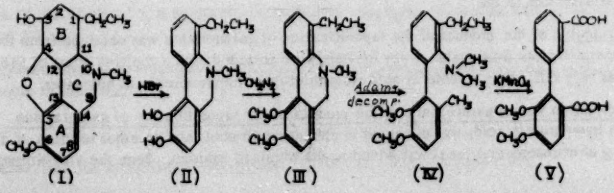


Absorption spectra. 1) Galantine; 2) galantimine.

As has been pointed out above, the function of one of the oxygen atoms of galantamine has remained unexplained. Attempts to obtain derivatives of the carbonyl group did not succeed; it is, therefore, very probable that the hypothesis on the presence of an ether-like bridge in galantamine is correct. Hence, naturally, in order to explain the structure of galantamine, it was necessary in the first place to carry out the splitting of this supposed bridge, which was achieved by the boiling of galantamine with strong hydrobromic acid in an environment of carbon dioxide. As a result of the opening of the ether-like bridge, we obtained a new optically inactive base with a clearly-expressed phenolic character. The base which was separated had the composition $C_{16}H_{17}O_2N$, m.p. 202-203°, and was considerably more difficultly soluble in organic solvents than galantamine, and was more easily converted into resin in the presence of alkali; it gave a well-crystallizing hydroiodide with a m.p. of 245.5-246.5°, and a hydrobromide with a m.p. of 228-230°. It contains two hydroxyl groups, but does not contain a methoxy group, or a reaction-inactive oxygen; its formula may be represented in the following way: $C_{15}H_{12}(NCH_3)(OH)_2$.

Further investigation of this substance led us to suggest that on the action of hydrobromic acid on galantamine, along with the saponification of the methoxyl group, the splitting of the ether-like bridge takes place, with the formation of hydroxyl groups, which is accompanied by the aromatization of one of the rings with the splitting off of two hydroxyls in the form of two molecules of water. This tendency of galantamine toward aromatization, characteristic for alkaloids of the phenanthridine series [5], is also a confirmation of the presence of this nucleus in galantamine.

All these considerations led us to Formula (I)* for galantamine; this formula explains the above given reactions very well.



* The position of one double bond is not shown.

Actually, the fact that the hydroxyl group in galantamine has a non-phenolic character indicates that it is found in the partially hydrogenated nucleus B. Position 4,5 may be considered most probably correct for the oxygen of the ether-like bridge; this is indicated by the ease with which it is split by acids like the furan ring. Further, taking into consideration that in natural substances, substituents usually occupy the ortho-position, it is possible to assume with a fairly large degree of probability that the hydroxyl group occupies position 3, and the methoxyl group, position 6. Taking into account the tertiary character of the nitrogen and the presence of the methyl imide group in galantamine, the latter may belong to the group of alkaloids of the phenanthridine series of the lycoramine type [6], which contain an ethyl group in position 1. As for the position of the double bond in galantamine, it is still unknown.

If we now turn to the product of saponification, obtained by the action of hydrobromic acid on galantamine, starting from the formula suggested by us for galantamine, we find that it may be represented by Formula (II). The separated product of saponification, as has already been mentioned, contains two phenolic hydroxyl groups, the presence of which is confirmed by their capacity for methylation with diazomethane. As a result of methylation, oily substance (A) was obtained, which was characterized in the form of its hydrochloride with a melting point of 217-218°, and its hydrobromide with a melting point of 228-230°, and which has the composition $C_{18}H_{21}O_2N \cdot HBr \cdot 0.5H_2O$ (III).

Along with oily substance (A) a small amount of crystalline base (B) with a melting point of 205-207° was obtained on the methylation with diazomethane of the product of saponification of galantamine; its hydrobromide had a melting point of 230-232°. The data on the analysis of this substance corresponds to a composition of $C_{17}H_{19}O_2N$. Substance (B) was not studied in more detail.

On the action of methyl iodide on substance (A), the methyl iodide compound of this substance, with a melting point of 144-150°, was obtained. Then, on the carrying out of the splitting of this methyl iodide compound by Adams' method, we obtained the oily product of decomposition (IV), with quite good yields. This substance gives a well-crystallizing hydrobromide with a melting point of 171-173°; the elementary analysis of the hydrobromide corresponds to the composition $C_{19}H_{25}O_2N \cdot HBr$. As a result of the oxidation of this base with permanganate in an acetone solution, a dicarboxylic acid with a melting point of 202-203° and a molecular weight of 333 was obtained. The data of the experimental analysis of this acid show a composition of $C_{16}H_{14}O_6$.

Thus, as might be expected on the basis of the formula suggested by us for galantamine, we obtained a dicarboxylic acid in which one of the carboxyl groups was probably formed on the oxidation of the ethyl chain at C_1, and the other on the oxidation of the methyl group at C_{14}; in addition to this, the oxidation is accompanied by the splitting off of the nitrogen, as a result of which, on oxidation, the dimethoxydiphenyldicarboxylic acid, shown on the scheme by Formula (V) is formed; we have called this compound galantaminic acid.

EXPERIMENTAL

The heating of galantamine with hydrobromic acid. To 12 g of galantamine was added 120 ml of 46% hydrobromic acid, and with the passing of carbon dioxide, the reaction mixture was boiled with a reflux condenser for 4 hours. Soon the entire precipitate went into solution. After the completion of the heating, a crystalline precipitate fell from the cooled solution; the precipitate was filtered and washed with alcohol. After recrystallization from alcohol, the hydrobromide (11 g) was obtained in the form of shining, flaky crystals with a melting point of 228-230°; they were quite difficultly soluble in cold water and more easily soluble in hot water.

The separation of base (II). 11 g of the hydrobromide of the saponified galantamine was dissolved in water, transferred to a separatory funnel, and shaken frequently on the addition of a solution of sodium bicarbonate by drops, in the presence of a large quantity of ether. The base, which was obtained after the distillation of the ether, in a quantity of 7 g, was composed of fine, colorless crystals with a melting point of 202-203°; the crystals were very difficultly soluble in water, ether and alcohol, and more easily soluble in chloroform.

Found %: C 75.10, 75.07; H 6.95, 7.00; N 5.90; OH 12.55, 12.32. $C_{16}H_{17}O_2N$. Calculated %: C 75.29; H 6.66; N 5.49; OH 13.33.

The hydroiodide of the product of the saponification of galantamine was obtained from the alcoholic solution; after recrystallization from water, flaky crystals were obtained with a melting point of 245.5-246.5°. The hydroiodide was very difficultly soluble in cold water and more easily soluble in hot water.

The methylation with diazomethane of the product of the saponification of galantamine. 7 g of galantamine, saponified with hydrobromic acid, was dissolved in anhydrous alcohol, and an ether solution of diazomethane (prepared from 12 g of nitrosomethyl urea) was added to the obtained solution. Soon the violent evolution of gas began.

The reaction solution was allowed to stand for 8-10 hours. On the driving off of the solvent, a quite mobile, oily mass with admixture of a small amount of crystals was obtained. On the addition of 40-50 ml of alcohol, the oily substance (A) went into solution; the crystalline substance (B), which is difficultly soluble in alcohol, was filtered from the alcohol solution.

The hydrobromide of base (A). The alcohol solution, after the separation of crystalline substance (B), was vacuum distilled, and to the oily basic residue, hydrobromic acid was added until an acid reaction was given of the reaction mixture. A fine, crystalline precipitate of the hydrobromide of substance (A) was formed. After washing with acetone and recrystallization from water, 4.6 g of the hydrobromide, with a melting point of 228-230°, was obtained.* On being dried in a vacuum at 110-120°, the hydrobromide lost 0.5 mole of water of crystallization, which was absorbed again on its standing in the air.

Found %: C 57.66, 57.30; H 6.47, 6.30; N 4.16, 4.17; OCH_3 16.61, 16.32. $C_{18}H_{21}O_2N \cdot HBr \cdot 0.5H_2O$. Calculated %: C 57.89; H 6.17; N 3.8; $(OCH_3)_2$ 16.62.

The hydrobromide of base (A) is very soluble in alcohol, acetone and hot water.

The hydrochloride. On the dissolution of the base of the methylated, saponified (with hydrobromic acid) galantamine in 10% hydrochloric acid, the colorless crystals of the hydrochloride were precipitated; they were filtered and washed with water; their melting point was 217-218°. The hydrochloride is very soluble in alcohol and in acetone.

The methyl iodide. 1.64 g of base (A) was dissolved in methyl alcohol, 3 ml of methyliodide was added and the reaction mixture was heated over a water bath for three hours. The fine crystals of the methyl iodide compound, which were separated on the driving off of the solvent, were washed with acetone, then with water. After recrystallization from water, 1.7 g of the methyl iodide with a melting point of 144-150° was obtained. The methyl iodide compound was quite soluble in alcohol and acetone, and more difficultly soluble in water.

The Adams' decomposition of substance (A). 1.6 g of the methyl iodide of substance (A) was dissolved with heating in water, and 5.26 g of 5% sodium amalgam was added gradually. After the addition of all of the sodium amalgam, the reaction solution was heated over a water bath for about twenty minutes, after which the solution, after being separated from the mercury, was extracted with ether. The residue, after the distillation of the ether, was a light yellow, quite mobile oily substance; 1.13 g of this substance was obtained.

The hydrobromide. To 1.13 g of the base of the product of the decomposition, a 10% solution of hydrobromic acid was added until the solution gave an acid reaction; the crystalline hydrobromide was isolated; it was then filtered and washed with water. After two recrystallizations from water, 0.53 g of the hydrobromide was obtained; it melted at 173-175° (at 170° it begins to decompose).

Found %: C 59.63; H 7.20; N 3.11; OCH_3 16.12, 15.57. $C_{19}H_{25}O_2N \cdot HBr$. Calculated %: C 60.0; H 6.78; N 3.69; OCH_3 16.31.

The oxidation of the product of the Adams' decomposition of substance (A). 1 g of the base of the product of the decomposition of substance (A) was dissolved in acetone, and to the obtained solution, a solution of potassium permanganate was added until a non-disappearing coloration was obtained. The manganese dioxide which was separated in this process was filtered, washed with acetone and then treated several times with hot water until the wash water did not give any additional precipitate with hydrochloric acid. The aqueous solution which was obtained in this way was evaporated until its volume was small, and, after the addition of hydrochloric acid until the solution gave an acid reaction, it was extracted with ether. The free acid, which was separated upon acidification in the form of a suspension, quickly formed an ester. The residue, after the distillation of the ether, was a mobile oily substance which gradually crystallized. The crystals were washed with ether and separated. 0.15 g of the acid was obtained; it melted at 199-201°. After the recrystallization from water of the obtained crystals, the acid melted at 200-203°.

Found %: C 64.17, 64.04; H 4.75, 4.56; OCH_3 17.23. M 333. $C_{16}H_{14}O_6$. Calculated %: C 63.57; H 4.63; OCH_3 20.53. M 302.

The obtained galantaminic acid was quite soluble in alcohol, acetone; it was difficultly soluble in hot water, and was almost insoluble in cold water.

* The base was isolated from the crystalline hydrobromide in the form of an oily substance.

The purification of base (B). The crystalline substance (B), obtained in small amounts on the reaction of the methylation with diazomethane of the galantamine which had been saponified with hydrobromic acid, was difficultly soluble in alcohol, and melted at 199-201°. After recrystallization from alcohol, its melting point was 205-206°.

Found %: C 75.08, 75.04; H 7.14, 7.16; N 5.30, 4.86. $C_{17}H_{19}O_2N$. Calculated %: C 75.8; H 7.06; N 5.2.

The hydrobromide. Base (B) was dissolved in 10% hydrobromic acid, whereupon the crystals of the hydrobromide of base (B) were quickly precipitated. After recrystallization from alcohol, the hydrobromide had a melting point of 230-232°. After repeated recrystallizations, its melting point was 235-236°.

SUMMARY

1. On the heating of galantamine with hydrobromic acid, the phenolic, optically inactive substance of the composition $C_{16}H_{17}O_2N$, its hydrobromide, and its hydroiodide were obtained.

2. On the methylation of the substance $C_{16}H_{17}O_2N$ with diazomethane, the oily base $C_{18}H_{21}O_2N$, its hydrobromide, hydrochloride and methyl iodide compound were obtained.

3. As a result of the reduction decomposition, by Adam's method, of the methyl iodide compound of the substance $C_{18}H_{21}O_2N$, an oily base whose hydrobromide had the composition $C_{19}H_{25}O_2N \cdot HBr$ was obtained.

4. On the oxidation of the product of the reduction decomposition with potassium permanganate in an acetone solution, the dicarboxylic acid of the composition $C_{16}H_{14}O_6$ was obtained; we called this substance "galantaminic" acid.

5. On the basis of the investigation which was carried out, the formula 1-ethyl-3-hydroxy-4,5-ethoxy-6-methoxy-N-methyltetrahydrophenanthridine has been suggested for galantamine.

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